

# net finishing

APPLICATION, ELECTRODEPOSITION, VITRIFIED ENAMELLING,  
ANODIZING, METAL SPRAYING, AND METAL FINISHING PROCESSES

Vol. 1, No. 1 (new series)

JANUARY, 1955

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JANUARY, 1955



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THIS JOURNAL IS DEVOTED TO THE SCIENCE AND TECHNOLOGY OF PAINT APPLICATION, ELECTRODEPOSITION, VITREOUS ENAMELLING, GALVANIZING, ANODIZING, METAL SPRAYING AND ALL METAL FINISHING PROCESSES.

THE EDITOR IS PREPARED TO CONSIDER FOR PUBLICATION ANY ARTICLE COMING WITHIN THE PURVIEW OF METAL FINISHING JOURNAL AND ALL SUCH ARTICLES ACCEPTED WILL BE PAID FOR AT THE USUAL RATES.

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## PATTERN FOR 1955

*I*N many respects both the art and practice of applying finishes to metal surfaces are of long standing, and such techniques as vitreous enamelling, hot-dip galvanizing, and painting have a long, distinguished and progressive history. In other respects the whole finishing industry has only recently achieved its majority and the application of scientific principles to finishing processes is of comparatively recent date.

Most of the technical organizations covering the metal-finishing field are young, albeit thriving, organizations, and there was for many years an apparent need for a virile technical journal to serve the needs of this flourishing and expanding industry.

The journal "British Industrial Finishing" later and better known as the "Industrial Finishing Journal" came into being in 1930, at a time when the commercial finishing of metal surfaces had reached a critical stage in its development as an industry in its own right, and it continued to do valued work in this field until, for a number of reasons, its identity was temporarily merged with one of its sister journals.

Since the war the technical development within the whole field of metal finishing has progressed at an ever-increasing rate and has expanded into new areas scarcely before conceived.

In the United States of America there has been for several years a very keen appreciation of the part played by a properly selected and applied finish in selling virtually each and every commodity, and this point of view is reflected in the strength of the finishing organizations in that country and of the technical press which supports them.

While full realization of this cogent fact is still not entirely universal in this country there is no doubt that there is more general appreciation of the fact that the cost of ensuring an attractive and effective finish on goods is recouped many fold in increased sales and enhanced reputation. It is thus at a time when industry is acutely aware of the technical problems attendant upon metal finishing and with the demand quickening for ever more technical information that METAL FINISHING JOURNAL re-appears on the scene, sharing the traditions of its sister journals as the product of an organization which, in many industrial fields today, has established a high reputation for competence and service.

In extending our greetings to all those engaged in the metal-finishing industry at the beginning of what promises to be a year of exceptional prosperity for this country, we look forward to playing our part in fostering the interests and broadcasting the achievement of this important technology.

# Talking Points

by "PLATELAYER"

TOPICAL COMMENT  
FROM THE MAIN  
LINES AND SIDE  
LINES OF METAL  
FINISHING

## OF THE MAKING OF BOOKS

**P**ROBABLY because of the rapid developments in industry and the great increase in facilities for technical education, there is a steady demand for new technical books. One of the difficulties in meeting this demand is the fact that often those having the knowledge and experience to write a really good book, do not seem to do so. This may be because of lack of time or inclination on the part of the potential author to engage in the arduous work of writing, proof-reading, correcting a manuscript, and ultimately wrestling with the Inland Revenue to retain a small proportion of the rewards of his labours. This situation accounts for some of the curious books which have been published in recent years on electroplating. About two years ago a text-book some 50 years old was reprinted in England and, presumably, sold to unsuspecting students of the subject. One is appalled to think, perhaps, of an aspiring electroplater in an outpost of civilisation struggling to produce a good deposit with current supplied by a Bunsen or Leclanché Cell constructed in accordance with the detailed instructions given in the book.

A recent text-book on the subject, not quite as bad, consists of an edited series of chapters made up entirely from trade catalogues and literature only, and makes very strange reading in parts.

When Kathleen Winsor, authoress of the amatory saga, "Forever Amber," was asked whether the volume was based on her own experiences, she replied, very wisely, "If I had had the experiences, I should never have been able to find the time to write the book." Apparently this applies to technology as well as scatology.

## NEW ANGLE ON METERS

It is often the most familiar things which could do with being improved, yet they go on unchanged for year after year with only very minor modifications. Take ammeters and voltmeters for example; a changed shape and a different dial is the most one has ever thought could be expected. Now a London firm has succeeded in giving a new slant to the meter business. The new instrument is an ammeter and a voltmeter combined in a single casing in such a way that the independent volt and ampere scales are located near the periphery of the dial chart, over which both indicating needles move, crossing at an angle as they do so.

The chart itself is formed by eight arcs which diverge from the point where the needles cross at zero loading. A series of numbered quadrilaterals divide the chart in such a way that with any particular constant resistance in the external circuit the needles always cross at a particular part of the chart.

In operation, the quadrilateral in which the needles cross for a given batch of work is noted by a skilled supervisor, and this determines the current required to give a specified thickness in a fixed time. For subsequent batches, it is only necessary for the operator to adjust the resistance panel or current regulator so that the needles cross in the same zone, when the same thickness of metal will be deposited on the second batch in the same time. This essentially simple device enables an unskilled operator to use a resistance board intelligently, and at the same time shows up any defects in the installation, such as an increase in resistance due to a vat leakage, bad connections, excessively worn or broken anodes, and so on.

## A BIT THICK

For years the industry has been searching for a reliable non-destructive thickness tester for electroplated coatings. Existing instruments based on magnetic attraction are subject to the limitation that either the coating or the base metal must be magnetic, whilst their accuracy may be upset by curvature and similar effects. Now the U.S. Bureau of Standards announces that they have developed no less than three electronic instruments for this purpose at one swoop. They all depend on measuring the difference in the electrical conductivity between the base metal and the coating. One of these instruments, typical of the three, the "Dermatron," utilizes the "skin effect," by which a high frequency eddy current is induced in the surface of the metal, and the resistivity of the surface layer is measured. As the coating and the base metal usually have different resistivities an indication of the deposit thickness can be obtained. Yet a fourth, we understand, is available in the United States, which is based on thermoelectric effects. It therefore looks as though there is no shortage of methods of achieving the desired results. The principal shortage is likely to be money since one thing is common to all these devices, i.e., they are all expensive, and are likely to be beyond the reach of the average plater.

# The Influence of SURFACE CONDITION

## on the GALVANIZING PROPERTIES of STEEL SHEETS

By HEINZ BABLIK\*

In this article the author, a well-known authority in the field of galvanizing, discusses the effect, due to cold rolling and impurity pick-up during annealing, on the zinc thickness obtained on sheets galvanized by the "dry" process, in baths containing aluminium.

ALTHOUGH the properties of the surface of the iron sheets used in galvanizing, from the point of view of physical and chemical structure, differ greatly from normal iron sheet there is still far too little consideration being given to the implications of this fact. This variation can mainly be attributed to two causes: viz. differing degrees of cold work frequently noticed on cold-rolled strip and the change which the iron base undergoes during annealing. The co-elements diffuse with varying rapidity in the iron and in the layer of scale which forms, so that—as is the case with silicon or copper—the iron surface is enriched. In addition the varying affinity for oxygen plays a certain part, and the author has proved that enrichment by silicon on the surface of sheets does take place, which in the course of certain galvanizing processes, leads to a considerable increase in the thickness of the zinc coating. This is because a certain content of silicon considerably increases the rapidity of the reaction between zinc and iron.

All of these superficial changes are particularly apparent in the process which is being employed exclusively for galvanizing sheets in Central Europe commonly known as "dry galvanizing". When correctly applied this process is distinguished by the fact that a reaction between iron and zinc does not take place during the period when the sheets are immersed in the zinc bath, thus preventing the formation of layers of iron/zinc alloy, i.e. the coating consists only of a layer of pure zinc. Due to this absence of a reaction between the iron base and the liquid zinc the entire reaction takes place in the surface layers, while in "wet" galvanizing the surface layer forms but a small part of the whole of the Fe used during reaction. The preservation of the particular superficial layer during the "dry-galvanizing"

process is essentially based upon two distinct causes, one of these being the method of fluxing used.

In the "dry-galvanizing" process no flux is used on the zinc bath, which is alloyed with aluminium, as flux containing zinc chloride would be reduced to aluminium chloride by the aluminium in the bath and, in this manner, would be speedily destroyed. Recently the author conducted tests which proved that this reaction could not be prevented even by adding sodium fluoride and other alkali salts. Thus with a bath which has been correctly alloyed with aluminium, the flux must be dried on the surface of the galvanized articles.

E. J. Daniels was able to prove (Table I.) that the iron base is far less liable to be attacked by zinc chloride than by molten zinc or the usual flux. In Table I. the loss is represented as being proportional to the square root of the duration of the reaction.

The results in Table I. however, only seem correct when relating to a process of diffusion,

TABLE I

Iron loss in gm./sq. in. dependant on the time of reaction, *t*, in minutes at 475° C.

| Melt  | Loss   |
|---|--|
| Pure $ZnCl_2$<br>$ZnCl_2 + 17\% NH_4Cl$<br>Zinc           | $V = 7\sqrt{t}$<br>$V = 375\sqrt{t}$<br>$V = 10.6\sqrt{t}$ |
| Reaction  | Loss   |
| $\frac{1}{2}$ min. in Salmiac flux<br>4 min. in Zinc bath | 260 gm./sq. in.<br>21 gm./sq. in.                          |

\*Gebr. Bablik A. G.

but are less correct when dealing with the reaction of a molten salt. For the purpose of comparison, however, it appears that given equal durations of reaction, the loss in weight caused by the molten "salmiac" flux is 50 times greater than that caused by molten pure zinc chloride. As can be seen from Table I, the loss in pure zinc is still greater than that caused by zinc chloride. Comparing the data quoted in the lower part of the table and the way they correspond to actual practical working conditions, it is found that if the iron sheets are left in the molten salmiac flux and in the zinc bath for a time, an appreciable weight of iron is removed; thus alterations in the physical structure or in the chemical composition of the iron surface occur less often during the usual "wet" galvanizing process, because the surface layers are removed by the effects of the flux and molten zinc. The author has previously proved (*Met. Ind.* 1951 Sept. 21,) that using the usual pickling process these superficially changed layers are not removed and that only a special pickle such as e.g. with nitric-sulphuric acids or electrolytic pickling can cause the changed layers to be removed.

An attempt to form, in Central European practice, a zinc coating which can withstand a considerable deformation without causing the coating to peel-off, has led to the alloying of the baths with aluminium, so that the aluminium concentration varies in accordance with the iron base. By adding aluminium, however, it is necessary to consider the fact that aluminium is oxidized from the bath more quickly than zinc, as immersion of the flux-covered goods leads to additional aluminium consumption. The correct aluminium content of the zinc bath must thus be tested at short intervals. Current practice for the production of coatings of the required flexibility is that such coatings are the better the thinner they are, i.e. the less they have been stressed, and it also follows that upon a thin iron base it is possible to have coatings that will withstand bending far better than those upon thick iron bases because the bending of the layer as compared with the neutral line of the coated sheet is greater on a thick iron base than upon a thin one.

During bending the zinc is actually deformed in the cast state, in which zinc shows a marked anisotropy. In addition the problem is further complicated by the fact that the zinc is a layer on the iron base and thus flakes away from it. It might be assumed however, that if an alloy forms between the base and the zinc then the zinc will not flake off.

When zinc coatings are deformed, it frequently occurs that the coatings develop cracks, which are only visible under a microscope but the zinc will not peel off the iron base because it firmly adheres to it due to an alloy-layer of iron and zinc. In

Fig. 1.— ( $\times 1200$ ) Section of zinc coating on wire produced by Crapo process



most cases, however, when the strength is low and the composition of the iron-zinc layers unsuitable, good adherence is not obtained, so that when strong iron-zinc layers are formed, the zinc coating will peel off when bent. On the other hand it is well known that with "galvannealed" coatings where the entire coating is built up by a layer of iron-zinc alloy, no peeling-off of the coating will occur during bending. This is because an efficient adherence to the iron base has been attained by the formation of these iron-zinc alloy layers.

The "galvannealed" coatings do not entirely peel off, even when they have small cracks in the surface. The author therefore does not agree with the results of the tests carried out by Hughes, who was of the opinion that a coating is perfectly bendable when it consists of only one alloy layer but that it bends badly when it consists of two or more layers. The results of Hughes are further disproved by the excellent "bendability" of Crapo wires which—as shown in Fig. 1—consist of a very strong layer of pure zinc next to a remarkably strong layer of iron-zinc alloy. During the Crapo treatment of the iron base a particularly adherent iron-zinc alloy layer is developed, so that the coating adheres exceedingly well to the iron base. A thin layer of pure zinc can be bent because the tensile strength of the cast metal is usually not exceeded. If, however, the zinc layer consists of iron-zinc alloys, the coating will not peel off because it is firmly fixed to the iron base.

The author has succeeded in proving the cause



of the inhibition of the reaction between iron and zinc in an aluminium-alloyed zinc bath. The inhibition effect is due to the fact that aluminium possesses a greater affinity for iron than for zinc, in consequence of which the aluminium present in the zinc bath primarily reacts with the iron base by forming an aluminium-iron layer. The existence of the aluminium enrichment in the iron may be confirmed by reference to Fig. 2. The spectra show the selective reception of the aluminium in the iron surface. It can be seen that in an Armco sheet the aluminium lines are not present, whereas they can be clearly recognized in galvanized Armco sheets from which the zinc coating has been removed by pickling. If pickling is continued still further, the aluminium lines eventually disappear. This is because the long pickling treatment has caused the complete removal of the surface layer. In the spectrum of the zinc layer the aluminium lines and, also one lead line can be seen. These illustrations appear to show beyond doubt the enrichment of the surface of the iron base by the aluminium.

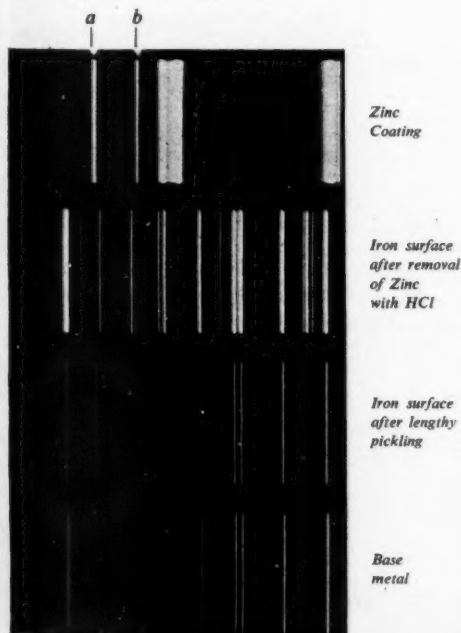
In Fig. 3 is shown another section of the same spectrum, which shows that the zinc-line 3345,0



Fig. 3.—Similar spectrogram as in Fig. 2 showing the region of zinc lines, demonstrating that by the treatment detailed in Fig. 2 the zinc coating has been entirely removed.

Fig. 2.—Spectrographic analysis of the surfaces of iron before and after galvanizing and the removal of the coating.

a=Al 3092 line b=Al 3083 line



which is far stronger in comparison with the Al line 3961,5 is not present; in this case the zinc coating has been removed by pickling, whereas the Al line was clearly present in Fig. 2. It is estimated that the Al diffusion attains a strength of about 3. It appears therefore that the iron-aluminium phase restricts the diffusion of the zinc, and is only eliminated when the Fe-Al phase is being transformed. This view is strengthened by the peculiar mechanism of the reaction as shown in Figs. 4 and 5. In Fig. 4 it can be seen that the reaction has been inhibited and in Fig. 5, which shows the central area of Fig. 4 at higher magnification, can be seen the crystals of the Fe-Al or Zn-Al phase. As long as these covering layers still exist, no reaction will occur there between iron and zinc. To the right and left of the central area, where the protective coating has been removed, a vigorous reaction has set in.

The correct amount of the Al addition must be determined not only with a view to the iron base but in consideration of the reaction produced by the flux. Aluminium has a far higher affinity for iron than zinc which leads to an enrichment of aluminium oxide at the places where the sheet is dipped. This Al oxide is not dissolved by the chloride of the zinc-containing flux in such a manner as to produce a melted fluid salt. In

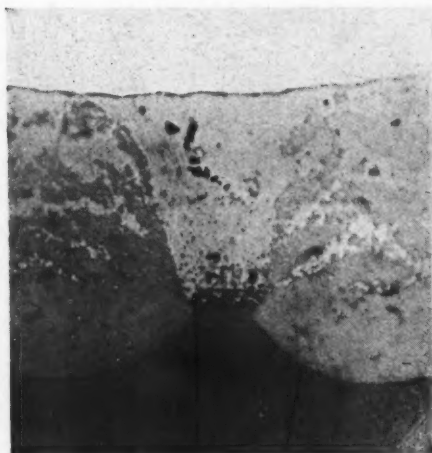


Fig. 4.—(Left) ( $\times 350$ )  
Section of zinc coating  
produced in zinc bath  
alloyed with aluminium

Fig. 5.—(Below left)  
( $\times 1200$ ). As in Fig. 4  
at higher magnification  
showing the Fe-Al-Zn  
phases

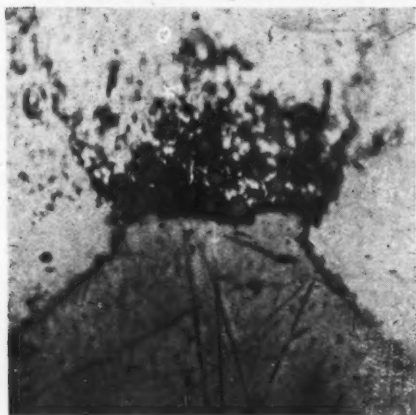


Fig. 6.— (Above  
right). Representa-  
tion at natural  
size of the de-  
wetting effect in  
a zinc coating.

Fig. 7.—(Right).  
( $\times 350$ ). Effect  
of presence of  
cementite re-  
vealed by oblique  
section of sheet  
(see Fig. 8)

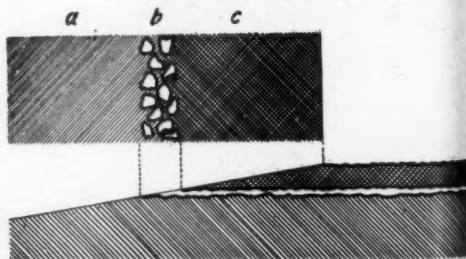


consequence, basic chlorides of metals will form and will stick to the surface as a flux residue. Galvanizing by means of baths having a high Al content therefore leads to certain difficulties with the flux.

By referring to the published work of Hoare in which he deals with sheets that are difficult to tin, the author was able to determine a phenomenon which is of great importance in galvanizing. Hoare, in the course of his research found that previously greased surfaces lead to the flowing-off of tin-coatings and he further stated that by degreasing and subsequent higher annealing, the flowing-off of tin coatings can be prevented. It is well known (as shown in Fig. 6) that the same effect can occur with zinc coatings. This flowing-off is caused by areas of cementite as shown in Fig. 7. In order to make the cementite visible, sheet surfaces were ground slantwise, as is shown in Fig. 8. It has been possible to produce cementite

artificially by covering Armco sheets with paraffin which is decomposed during annealing in the absence of air. In this way surface cementite has been formed (Fig. 9). A further method of

Fig. 8.—Diagrammatic representation of oblique section through cementite layer on iron sheet  
(a) iron (b) cementite (c) scale





producing this type of cementite consists in applying postassium ferrocyanide to the surface (Fig. 11). By annealing paraffin-coated sheets in an atmosphere of town gas it has also been possible to produce this cementite. All of these methods of treatment lead to the formation of cementite on the surface of the sheets as represented in the cross-section in Fig. 10.

In addition, all of these methods of production require the application of carbon to the surface of the sheets, followed by heating so that the iron reacts with the carbon to form cementite. In this process the reaction temperature must be such as to enable a reaction to occur between the iron and

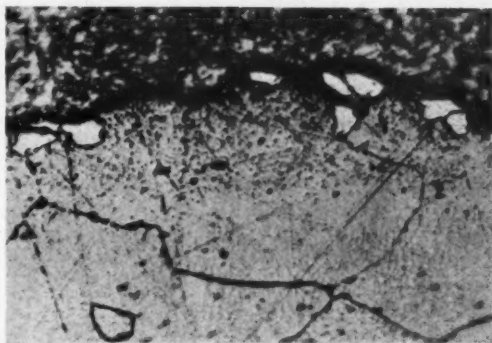


Fig. 9.—(Left). ( $\times 350$ ). Surface cementite produced in sheet by annealing paraffin-coated sheets in a reducing atmosphere

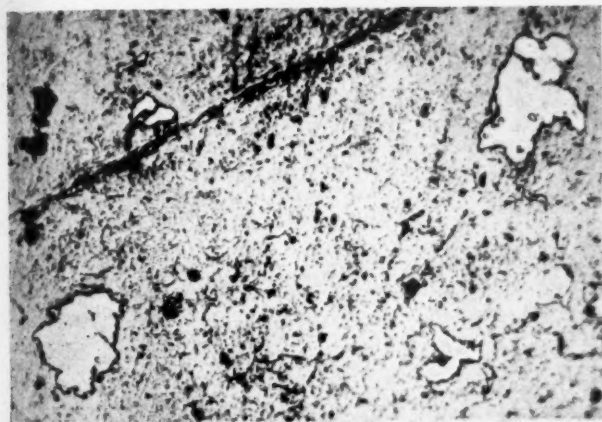


Fig. 10.—(Above). ( $\times 350$ ). Section of sheet shown in Fig. 9 revealing presence of grains of cementite

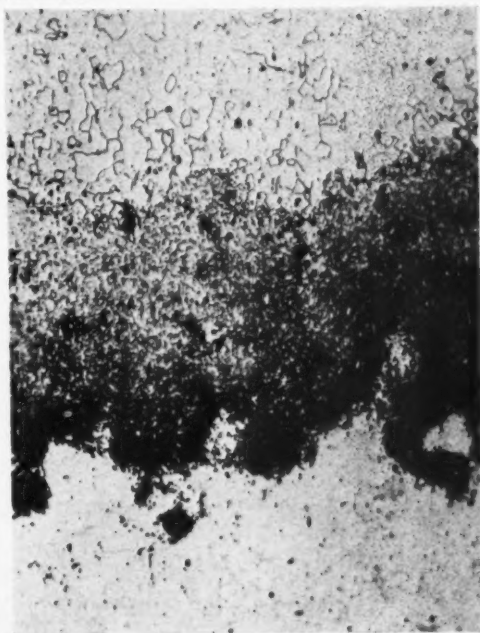
Fig. 11.—(Below). ( $\times 120$ ). Oblique section of sheet treated with potassium ferrocyanide. Top: Ferrite; centre: Braunit; right: Cementite

carbon but should be low enough so that the rate of diffusion of the carbon in the iron is not great.

In practice, however, subsequent tests have shown that when sheets are hot-rolled, the surfaces do not become greasy and are not contaminated with graphite or other carbon-containing materials neither are they handled in a non-oxidizing atmosphere so that for the present the author has not succeeded in explaining the formation of cementite areas on normal production sheets. A tempering treatment with  $K_4FeCN_6$  leads to an almost uninterrupted pearlitic intermediate layer and a cementite layer as shown in Fig. 11; the continuous cementite layer prevents "wetting" of the iron during galvanizing.

It is remarkable that in practice the cementite forms mostly at the corners of the sheets, as can be seen in Fig. 12. This type of distribution indicates that the formation of cementite is in some way connected with annealing, i.e. without a protective atmosphere.

The author has previously proved on a sample of supereutectic pig iron (*Korrosion und Metall-schutz*, 1945, (1-2) page 5) that with this iron the reaction between iron and zinc is considerably retarded due to its high carbide content. It must



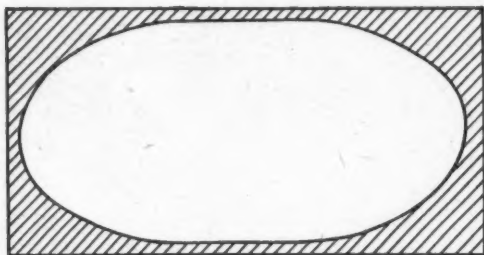


Fig. 12.—Diagrammatic representation of area (hatched) of preferential cementite formation

be assumed therefore that with zinc baths alloyed with Al the reaction is retarded still more and because of the relatively large amount of cementite on the iron surface its "wettability" is very low, thus causing the zinc to flow off the surface of the iron sheets.

Annealing of sheets showing this phenomenon, with exclusion of air, at about 820 to 860°C. causes this cementite to disappear from the surface; it probably diffuses into the interior of the sheets. While sheets which have been annealed at too low a temperature, in Al-alloyed baths show the phenomenon of the zinc coating flowing off in the shape of tear-drops, other sheets which have been annealed sufficiently long at a higher temperature never show this effect. Also, normally annealed sheets, which pass singly through the

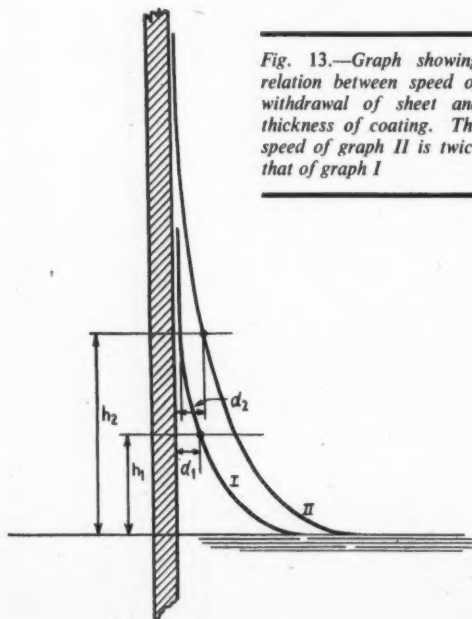


Fig. 13.—Graph showing relation between speed of withdrawal of sheet and thickness of coating. The speed of graph II is twice that of graph I

annealing furnace, and which have a thick, even scale do not show the phenomenon of "tears." However, as has been stated above, in this case the higher annealing temperature has to be considered. Recently Wüster and Horstmann in *Stahl und Eisen* have explained the phenomenon of the flowing off in tear-drops by declaring that this phenomenon is bound to occur when the iron base is still carried on oxide film.

The author does not agree with this opinion and does not consider it necessary to quote reasons in detail, because every galvanizer will see that these explanations are at variance with all the known facts of the case. The formation of the "tear-drops" must not be confused with the insufficient wetting of the iron surface, caused by the evolution of hydrogen during the crystallizing of the zinc. It is well known that with the presence of sulphur or phosphorus segregations, or oxide deposits in the sheets, an increased pick up of diffused hydrogen occurs; here also, the roughness of the iron base plays its part. A major part of the diffused hydrogen is expelled from the iron by the heating occurring during the galvanizing process. Naturally such an iron surface covered as it is with hydrogen bubbles cannot easily be wetted and thus the zinc coating on such an iron base cannot flow sufficiently to form a good coating.

If the enrichment by hydrogen happens locally, pickling spots will be formed; if the evolved hydrogen is distributed over the entire sheet, the latter acquires the appearance known as "grey sheet."

Another also highly unwelcome phenomenon which occurs when galvanizing in Al-alloyed zinc baths, is the occurrence of the phenomenon shown in Fig. 13, which is connected with the viscosity and surface tension of the zinc bath and is a function of the speed of removal or similar factors during the dipping operation.

From Fig. 13 it can be readily understood that depending on the exit speed more or less zinc is carried off with the iron sheet. But because of the thick zinc coatings, which occur when the sheets are rapidly taken from the bath, not being able to adhere permanently to the iron surface, the coating flows off downwards, i.e. opposite to the direction of removal from the bath and on solidification forms the "curtain-like" zinc coating.

The Al content undoubtedly plays a major part in this phenomenon, because the skins of Al which form upon the surface of the bath not only influence the viscosity of the bath but also the surface and flow of the zinc.

Thus the addition of Al to the zinc bath can cause many practical difficulties which to date have not yet been overcome.

# Recent Developments in

Abstracted from a paper presented to a meeting of the London Branch of the Institute of Metal Finishing held at the Northampton Polytechnic on December 13, 1954

## CHROMIUM PLATING

By H. SILMAN, B.Sc., F.R.I.C., F.I.M., M.I.Chem.E.

THE fundamental principles governing the plating of chromium from chromic-acid solutions were established about 25 years ago by Liebreich (1) and by Fink (2) and form the basis of the methods which are almost exclusively used nowadays for the commercial electroplating of the metal. To deposit chromium from trivalent chromium solutions has been the object of a great many investigators, but the difficulties of pH control and the fact that the chromium-anodes do not dissolve in the bath have proved insurmountable for the deposition of the metal for decorative or industrial applications. For electrowinning, however, methods of deposition from trivalent baths have been employed successfully (3) using a solution containing a mixture of sodium sulphate, chromic acid and chromic sulphate with insoluble anodes which are surrounded by an asbestos diaphragm to prevent the oxidation of the chromium salts to the hexavalent state.

### Solutions

For most, but by no means, all industrial applications the solutions used consists of chromic acid with a small proportion of sulphuric acid which acts as the catalyst. The concentration of sulphuric acid is not highly critical, but the ratio of chromic to sulphuric acid is most important. In general about 40-80 oz. per gal. of chromic acid is used with sulphuric acid in the proportion of around 1 per cent by weight. The usual range is a chromic / sulphuric acid ratio of between 120:1 and 80:1 while anodes are of antimonial or tin-lead, and should be designed to have high current-carrying capacity (Fig. 1). Plating is carried out at 95-115°F, depending on the concentration of the bath and the type of deposit required. The cathode efficiency is low, averaging around 12 per cent.

### Plant

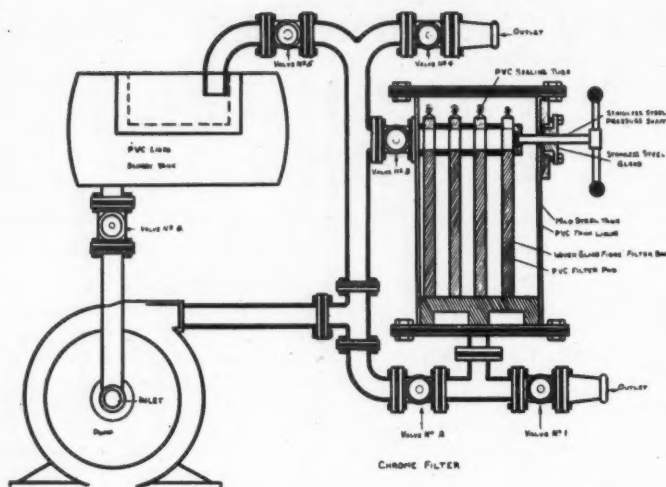
Chromium-plating tanks are usually made of antimonial-lead lined steel heated by an external water-jacket. Glass sheets are attached as an inner loose lining on the sides and bottom of the tank to prevent short circuiting and to prevent the lining becoming electrified. Exhaust equipment

is essential and is a legal requirement. An additional method of reducing spray is to float small hollow polythene tubes on the solution surface, or, even better, to add a suitable surface active agent to reduce the surface tension of the solution. The difficulty here is to find a material which will not be decomposed by the highly oxidizing solution. A recently developed organic fluorine derivative appears to have a longer life in the plating bath than any hitherto available and has found considerable application. It has no effect on the plating characteristics of the bath itself, unless considerable thicknesses are being deposited, when some pitting may occur. Filtration is not common but is useful in preventing nodulation where heavy deposits are being built up. Filters and pumps for this purpose are best made of polyvinyl chloride, or lined with it, satisfactory filter cloths or gauges being either of the same material in woven form, or of Terylene which gives a finer degree of filtration. A filter and pump unit for chromium solutions is shown in the diagram in Fig. 2.

### Alternative Catalysts

Recently there has been a greatly increased interest in chromium solutions containing fluorides, fluosilicic acid and borofluorides with or without the presence of sulphuric acid (4). These have the advantages of superior throwing power and greater current efficiency while the bright plating range is much wider and hard bright deposits can in fact, be obtained in cold solutions of this type. They are also capable of withstanding breaks in current during the plating process, which, in the case of the sulphate-catalyzed electrolyte usually results in dull or poorly adherent deposits.

The fluoride-type baths however are rather more difficult to control, and analysis is more complicated. They are also more aggressive towards tanks and tank linings, plating jigs, anodes and unplated surfaces of articles being processed, resulting in the undesirable accumulation of heavy metals in the solution. The catalyst most commonly employed in this type of bath is hydrofluoric acid, or hydrofluosilicic acid, the



ratio of chromic acid to catalyst varying from 150:1 to 300:1.

Cold chromic-plating baths based on fluoride-catalysts are used quite extensively in Japan (<sup>5</sup>), the activating agent being chiefly ammonium fluoride, one of the more widely used electrolytes being that described by Tajima (<sup>6</sup>).

Sulphate-free barrel-plating solutions have been investigated by Dubpernell and Martin(<sup>7</sup>) and McNair(<sup>8</sup>), while a fluosilicic-sulphuric acid catalyzed electrolyte has been studied by Wahl & Gebauer(<sup>9</sup>).

#### Self-regulating bath

Of outstanding interest, particularly in the United States, and to an increasing extent in this country, is the self-regulating type of solution(<sup>10</sup>) the commercially available form of which is known as the S.R.H.S. bath, based on sulphates and silicofluorides as the catalysts. Control of the catalyzing acid is achieved by the inclusion of a salt mixture which has the solubility needed to maintain the correct concentration of catalyst in the bath(<sup>11</sup>). An excess of the salt is added with chromic acid and this remains in the bath in the undissolved form.

If the concentration of catalyst falls the requisite amount goes into solution, and cannot be exceeded. Analytical control of the chromic-acid content only is therefore all that is necessary.

There are numerous patent claims for self-regulating baths. One type of solution which has received considerable commercial application(<sup>12</sup>) contains 2 per cent of strontium sulphate, 5.5 per cent of potassium silicofluoride and 92.5 per cent of chromic acid. The chromic-acid concentration ranges from 150-500 gm. per litre depending on the application for which it is required. For decorative

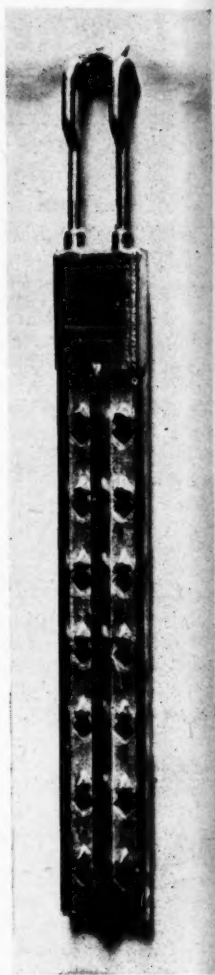
Fig. 1.—(right). Heavy-duty chromium-plating anode, available either in antimonial-lead or tin-lead alloy as required.

Fig. 2.—(above). Diagrammatic representation of pump and filter equipment for chromium-plating solutions.

[Courtesy Silvercrown Ltd.]

plating a temperature of between 95° and 125°F. is employed. The S.R.H.S. solution has considerably better covering power than the sulphate-type and is also said to be capable of dealing with passive nickel, stainless steel or stripped articles more satisfactorily.

Owing to the higher cathode current efficiency resulting from the presence of the silico fluoride catalyst and the wide bright plating range of the bath, plating speeds can be up to 50 per cent greater than with the ordinary bath, particularly in the regions of higher current density and temperature. The deposits obtained from the S.R.H.S. bath are generally smoother, finer-grained and more free from imperfections and cracks than those from the conventional baths. The relative absence of cracks is probably also the basis of the claim that the fatigue of steel is reduced to a lesser extent by chromium plating from the S.R.H.S. bath than from the conventional solution. Fig. 3 shows the improved efficiency of the bath.





### "Crack-free" process

A recently introduced modification of the S.R.H.S. bath produces a deposit which is substantially free from the cracks which are a normal characteristic of most chromium plating<sup>(13)</sup>. The solution may contain 200-900 gm. per litre of chromic acid and is operated at 150°F. and a current density of about 400 amp. per sq. ft. Under these conditions the rate of deposition is between .00065 in. and .0015 in. per hour, and the deposits are matt or semi-bright but can be buffed to a fully bright finish, as they have a D.P.H. of 435-700. The corrosion resistance is considerably superior to that of normal chromium as shown by exposure and salt-spray and are also claimed to have considerable levelling action.

### Plant Requirements

As the fluoride and fluosilicate baths are more corrosive than the sulphuric-acid solutions, precautions have to be taken accordingly. Although antimonial lead lined tanks, such as are normally employed in chromium plating, can be used, 7 per cent tin-lead alloy linings have been recommended as being superior in resisting solutions of this type.

Plastic linings, particularly polyvinyl chloride, can be obtained which are fully resistant to the solutions, but their use is not altogether simple as blistering of the lining tends to occur, especially around the water line of the heating jacket due to temperature differentials. In this respect the newer two-ply plastic linings, with an intermediate plasticized polyvinyl-chloride layer bonded to the steel and an unplasticized polyvinyl-chloride layer in actual contact with the solution are useful.

Internal steam heating coils of antimonial- or tin-lead are employed almost exclusively now in the U.S.A.

### Sodium-tetrachromate Bath

The tetrachromate bath developed by Bornhauser has received a limited application for depositing chromium directly onto zinc<sup>(14)</sup>. The solution contains caustic soda in addition to chromic acid, so that sodium tetrachromate is formed. A typical solution contains 400 gm. per litre  $\text{CrO}_3$ , 58 gm. per litre  $\text{NaOH}$  and 0.75 gm. per litre  $\text{H}_2\text{SO}_4$ . High current densities can be used (200-800 amp. per sq. ft.), the current efficiency being 30-35 per cent. Anodes are of antimonial or chemical lead, and a high anode-cathode ratio is recommended. If the bath temperature is maintained at 60-70°F. by cooling, current densities of 500 amp. per sq. ft. can be maintained and deposits of .003 in. can be obtained in one hour (corresponding to a current efficiency of around 30 per cent). At temperatures in excess of 75°F. the sodium tetrachromate begins

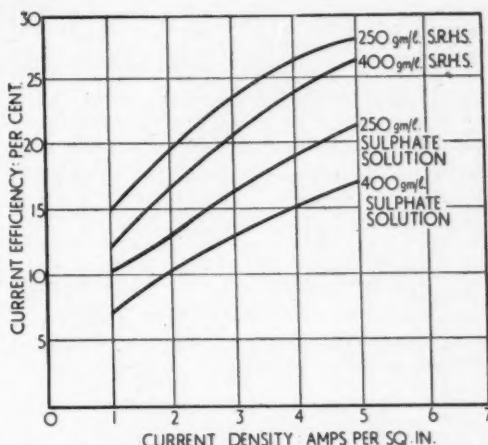


Fig. 3—Curves showing the relative efficiencies of S.R.H.S. and sulphate chromium baths

to decompose, being completely dissociated at 100°F.; thus proper arrangements must be made for keeping the solution cool during working. The deposits from this bath are soft and matt, but can be readily polished, the resulting appearance approaching that of normal bright chromium plate. A wide plating range can be used, since this is not limited by the somewhat narrowly restricted conditions under which the sulphuric-acid catalyzed bath will produce a bright deposit.

A commercial version of the Bornhauser solution has found some application in Germany where it is known as the "D" process<sup>(15)</sup>. It uses interrupted current, and is recommended for direct chromium plating onto brass castings and stampings, zinc, aluminium, and also steel. Current densities of 500 amp. per sq. ft. can be employed to deposit .00002 in. in 4-6 minutes.

### Corrosion-resistant chromium deposits

Although chromium itself is highly resistant to corrosion by the atmosphere and by many chemicals, the structure of the electrodeposited metal is highly fissured, which reduces the protective value of the coating considerably.

In some work carried out by Dettner<sup>(16)</sup> cylindrical steel bars plated with chromium under different conditions were subjected to accelerated corrosion tests. This work indicated that the lowest corrosion resistance occurs at current densities of around 750 amp per sq. ft. and temperatures of 53°C. Both increasing or decreasing the bath temperature from the minimum point have the effect of increasing the corrosion resistance. At temperatures above the zone of minimum corrosion resistance (45-58°C.) raising the current density reduces the corrosion resistance

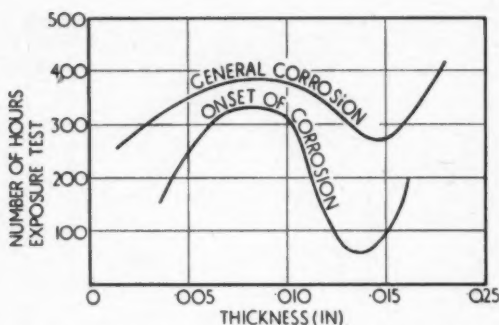


Fig. 4.—Graph showing the influence of deposit thickness on corrosion resistance of chromium plate.

while at temperatures below this minimum region the effect of increasing the current is in the opposite direction. Hence it is seen that the most corrosion-resistant coatings are produced at high bath temperatures and low current densities, but this is outside the bright plating range of the solution. (Fig. 4).

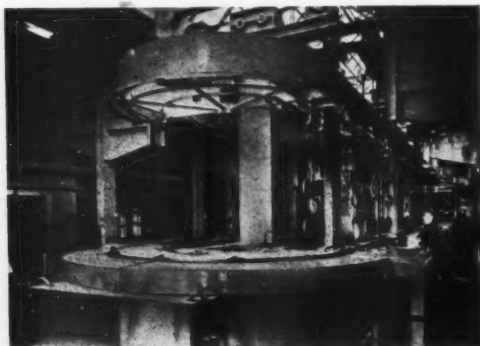
Temperatures of 60° C. and current densities of around 400 amp per sq. ft., however, enable bright deposits to be obtained, and these have been found to have increased corrosion-resistance on atmospheric exposure tests, when used in the conventional thicknesses for decorative chromium plate. There is little reduction in cathode efficiency under these conditions, but the throwing power of the bath may be slightly inferior.

#### Barrel Chromium Plating

Many attempts to build satisfactory barrels for chromium plating small parts have been made. One of the first successful machines was built in Germany about 1938 and consisted of a partially

Fig. 5.—Modern automatic bright nickel- and chromium-plating plant for automobile hub-caps.

[Courtesy Electrochemical Engineering Co., Ltd.]



immersed horizontal barrel containing a helix, so that the articles travelled horizontally through it, being discharged at the far end. Several types of modern barrels are now available, mostly based on a similar principle, and are capable of producing fully bright deposits. A certain amount of "burning" or "missing" is, however, inevitable, and the articles must be individually inspected after plating. The proportion of defective work need not be excessive, if care is taken in controlling the plating conditions and selecting the type of articles to be plated in the barrel.

Silicofluoride solutions are used in barrel chromium plating, sometimes with air agitation, since they have a wide plating range and withstand current interruptions more satisfactorily than sulphate solutions.

It is desirable that there should be the minimum of delay between nickel and chromium plating. If delay has occurred, an activating dip in sulphuric or nitric acid may be advisable.

#### Tampon Plating

An interesting recent improvement in the technique of applying local deposits of chromium, especially for engineering applications consists in applying the solution by a rubbing action to the article being plated by means of an inert anodic electrode attached to a pad impregnated with the plating solution, with the article to be plated being cathodic. Suitable plating solutions are based on an organic amino-oxalate salt of chromium, such as Gregory's salt  $\text{Cr}(\text{C}_2\text{O}_4)_3(\text{NH}_4)_3$  dissolved in an alcohol such as methyl alcohol with an alkyl amine wetting agent.<sup>(17)</sup>

Very high current densities are employed so that the solution boils away in use and is replenished from time to time. The electrolyte is slightly alkaline and is non-corrosive to the skin or to the metal being plated. Current densities of up to 4000 amp. per sq. ft. can be used and the metal is deposited at the rate of .00001 in. per minute. The deposits are bright and adherent.

A graphite rod is used as the electrode to which the pad is attached and this can be water-cooled if need be.

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## INSTITUTE OF METAL FINISHING

### ANNUAL GENERAL MEETING

THE annual general meeting of the Institute of Metal Finishing was held at the Grand Hotel, Sheffield, on November 26, 1954. The meeting opened with the presentation by the Hon. Treasurer of the statement of accounts for the year ended June 30, 1954; a deficit of nearly £200 was noted for the year's working.

The annual report of Council was then presented by the hon. secretary, Dr. S. Wernick, who stated that ordinary and corporate membership of the Institute had increased during the year. He said, however, that although the membership figure was encouraging, there was no doubt that the potential membership was considerably greater than that indicated by the net figure. Individual members could help the Institute by bringing the attention of friends and colleagues to its aims and objects, with a view to their enrolment as members in their own right. Dr. Wernick said that in the previous annual report he had recorded an admirable increase in the number of technical meetings held, mainly due to the formation of the North West and Scottish Branches and the Organic Finishing Group. All these sections had now got into their full stride and a further increase in technical meetings had resulted. He made special reference to the meetings addressed by the Institutes' Hothersall Memorial Medallist, Dr. William Blum, including which the total number of meetings of the Institute reached the figure of 50.

The Organic Finishing Group had fully justified the considerable effort entailed in its creation in March, 1953, when the inaugural meeting was held in London, and under the chairmanship of Mr. A. A. B. Harvey, and with Mr. J. N. T. Adcock as hon. secretary, five meetings, alternating as to venue between London and Birmingham, were held during the year under review.

After paying tribute to the work of the branches, the hon. secretary then made reference to the special meetings of the Institute. In particular he referred to the Hothersall Memorial Lecture, and said how glad the Institute was to welcome Dr. Blum immediately preceding the other major function held by the Institute, viz. the International Conference. It was appropriate Dr. Wernick said, that Dr. Blum should be able to give his lecture at a time when so many of his compatriots would be present in this country.

Members of the Institute who were not able to hear Dr. Blum's address were nevertheless able to meet and hear him as a result of a lightning tour which he made subsequent to the International Conference.

Dr. Wernick then said that the International Conference was held in this country under the aegis of the International Council for Electrodeposition, the constituent members of which are, in addition to the Institute, the American Electroplaters' Society, and the Commission Belge de l'Électro-Déposition.

The considerable amount of work involved, the Institute being the host, proved to be fully justified and the response from all overseas countries was most gratifying, a total of 509 delegates attending from 14 countries. Seven technical sessions were held at which 32 papers were presented. The American Electroplaters' Society was to organize the next International Conference, which will be held in Detroit, in 1959.

Referring briefly to the Institute's publications, and to works visits and social functions, Dr. Wernick then gave details of the Institute's Awards other than that to Dr. Blum. No award of the E.T.S. Gold Medal or the Johnson Matthey Silver Medal had been made, but on the recommendation of the publications committee, the Westinghouse Brake and Signal Co. Ltd. Prize was awarded to Dr. A. E. Davies, Mr. R. M. Angles and Dr. J. W. Cuthbertson for their paper on "Complex Fluorides for the Deposition of Tin and Tin Alloys."

Finally Dr. Wernick said that the Council had, with regret, found it necessary to increase the membership subscription to 3 guineas, due mainly to the increasing amount of technical matter now being published by the Institute, and then paid tribute to the work of all executives of the various branches, members of committees and sub-committees, and to the Institute's staff at headquarters.

#### OFFICERS AND COUNCIL

The Council appointed the following officers for the 30th Session, 1954-55:—

##### President:

Professor J. W. CUTHBERTSON, D.Sc., F.I.M., A.M.I.E.E.

##### Immediate Past President:

H. SILMAN, B.Sc.(Lond.), F.R.I.C., M.I.Chem.E., F.I.M.

##### Vice Presidents:

S. G. CLARKE, D.Sc., Ph.D., A.R.I.C., F.I.M.  
G. E. GARDAN, Ph.D., A.R.C.S., F.R.I.C., F.I.M.  
R. A. F. HAMMOND, B.Sc., A.R.C.S., F.R.I.C.  
T. P. HOAR, M.A., Ph.D.(Cantab.), B.Sc.(Lond.), F.R.I.C., F.I.M.

R. W. NICOL

E. A. OLLARD, A.R.C.S., F.R.I.C., F.I.M.  
C. WHARRAD.

(continued in page 42)

# Alternatives to NICKEL under CHROMIUM Plate

## Final Report to Committee of Co-operative Groups

### Formation of the Group

THE "CODAF" (Co-operative Development of Alternative Finishes) Group was formed in January 1952 to help meet the situation created by the shortage of nickel supplies to the metal-finishing industry. It represented an attempt to bring together technicians from a number of the larger manufacturing companies interested in electroplating, in order to pool technical resources and knowledge and to attack jointly the serious problems then facing the industry. There was at that time no other body whereby this could be achieved.

The following companies comprise the Group:

The Birmingham Small Arms Co. Ltd., including the Small Heath and Waverley Works, and the B.S.A. Group Research Centre,

Guest, Keen and Nettlefolds Ltd., including the Ionic Plating Co. Ltd., and the G.K.N. Group Research Laboratory, Humber Ltd.

Morris Motors Ltd., including the Radiators Branch and the Nuffield Central Research Laboratories.

Joseph Lucas (Industries) Ltd., was associated with the Group during the first year of its existence.

Liaison was established with the British Non-Ferrous Metals Research Association, which at about the same time took in hand a research project on possible substitutes for normal nickel or chromium plate, more particularly on the extent to which copper could replace nickel as an undercoat to a chromium finish. Representatives of the Association attended all Committee meetings of the Group as observers and received all Minutes and Reports. This arrangement proved of much value in the deliberations of the Group.

### Work Done by the Group

Reports on all work done by member companies on possible alternatives to the usual nickel-chromium-plate prior to formation of the Group, were immediately made available to members. From these reports, a summary and comparison of alternative finishes was prepared. A survey was also made of the laboratory and process facilities available in the works of member companies. From this information, the most

promising lines of progress by joint action emerged, and it was seen that the further work required would take the form both of laboratory investigations and of development work on the industrial value of known processes.

The following programme was agreed on and was allocated as shown:

| Process  | Company   |
|--|---|
| <b>Bronze Plating</b>  |   |
| General Investigation of Process                                     | B.S.A. Co. Ltd.                                 |
| Investigation of Barrel Plating                                      | Ionic Plating Co. Ltd.                          |
| Examination of Commercial Samples                                    | Humber Ltd.                                     |
| <b>Modified Chromium Plating</b>                                     |   |
| High-Temperature Sulphate Bath                                       | Joseph Lucas (Inds.) Ltd.                       |
| Solutions containing Radicals other than or in addition to Sulphates | Joseph Lucas (Inds.) Ltd.<br>Morris Motors Ltd. |
| <b>P. R. and Bright Copper Plating</b>                               |   |
| Experimental Investigation   | Humber Ltd.                                     |
| <b>Lacquered Finishes</b>  |   |
| Completion of Previous Work  | Humber Ltd.<br>Morris Motors Ltd.               |
| <b>Wax-Sealed Finishes</b>   |   |
| Completion of Previous Work  | Morris Motors Ltd.                              |
| <b>Tin-Nickel Plating</b>  |   |
| Process Investigation  | Ionic Plating Co. Ltd.<br>Morris Motors Ltd.    |

As and when stages in the completion of this programme were reached, the company concerned made its report available to members of the Group. Altogether, some 22 such reports were distributed.

At the end of the first year's operation, however, the further work done in that time by member companies was reviewed and effort was then concentrated on selected processes.

It became possible, too, at this stage to put before the Metals Economy Advisory Committee of the Ministry of Supply certain recommendations as to the essential need for having at least a thin deposit of nickel immediately beneath a chromium finish if the basis metal were to be adequately protected. These recommendations were helpful in accelerating the relaxation of the restrictions on uses of nickel in the plating trade.

In order to obtain some approximately quantitative comparison of the relative protective values of the more promising combinations of undercoat and finish being explored but hitherto

tested under different conditions by the companies that originally reported on them, atmospheric exposure tests were carried out at four selected sites, representing a wide range of corrosive conditions. Exposure was continued for seven months.

In addition to this main programme, two other investigations were carried out. First, the possibility of adapting the C.R.L. Preston and Stroud sulphur-dioxide test for paint films to the testing of plated coatings was studied. In this work, a comparison was made between the results of exposure to industrial atmospheres and the results of exposure to a sulphur-dioxide atmosphere as produced artificially in the modified procedure for the test now being developed by the Institute of Petroleum. The method was found useful in distinguishing, in a matter of days, between promising plated finishes and those not deserving further study. At its present stage of development, however, the test still leaves something to be desired in the classification of plated coatings.

Second, it having been suggested that electrodeposited antimony might serve to replace nickel as an undercoat to a chromium finish, the merits of the various baths recommended for the electrodeposition of antimony were examined. None of the antimony deposits from known solutions were sufficiently ductile and adherent to promise commercial application. Further, it was confirmed that electrodeposited antimony forms a brittle alloy by diffusion into a copper base.

#### Conclusions from Exposure Tests and Practical Trials.

**Bronze Undercoat + High-Temperature Chromium Finish.**—From the point of view of atmospheric corrosion-resistance alone, a "Lucas" high-temperature chromium finish, approximately 0.00004 in. thick, over a 10-12 per cent. tin-bronze undercoat, approximately 0.0010 in. applied by one of the available proprietary processes, is greatly superior to any of the other combinations tested by the Group. This superiority is largely due to the chromium, but the same finish over a copper undercoat is much less successful, indicating that the bronze contributes to the value of the combination.

The colour of this combination, however, is not equal to that of a normal chromium finish over nickel. Whatever the undercoat next to the steel, at least a thin deposit of nickel below the chromium would appear to be essential to the production of a chromium finish of the "traditional" colour.

Furthermore, operation of the high-temperature chromium plating process on an industrial scale

offers a number of practical difficulties. In particular, under the conditions of working, the throwing-power of the solution is inferior even to that of the same bath as normally operated for decorative deposits, jiggling or racking is a decided problem, and the risk of "burns" and "misses" is greater. Moreover, for the best effect, the deposit usually requires a final polish even though this operation is a light one.

**Bronze + Sub-Standard Nickel + Normal Chromium.**—A normal chromium finish with a nickel undercoat approximately 0.0002 in. thick (i.e., less than that specified in British Standard 1224:1945\* for plated steel exposed to severe outdoor conditions) over an undercoat of 10-12 per cent. tin bronze approximately 0.0010 in. thick applied by the proprietary process referred to, has considerable merit, except perhaps under the most severe conditions of use. In order, however, that the full benefits of this combination may be obtained, the operation sequence and type of nickel bath must be carefully chosen to ensure sound adhesion between the composite layers.

**Copper + Tin-Nickel.**—A tin-nickel-alloy finish, applied under the best conditions over a copper undercoat, has all the corrosion-resistance claimed for it, but when used out-of-doors where dust accumulates, the finish loses its bright and attractive appearance very rapidly as compared with normal nickel-chromium plate. It is thought that, when nickel is in adequate supply, the finish is not likely to compete with nickel-chromium plate for outdoor applications. For indoor purposes, a tin-nickel finish is attractive and serviceable.

**Sub-Standard Nickel + Chromium + Wax Seal.**—The decorative and protective value of a normal chromium finish, sealed with a selected wax, over an undercoat of nickel of thickness approximately half that recommended in British Standard 1224:1945\* for plated steel exposed to severe outdoor conditions, compares very favourably with that of the same finish, unsealed but with the specified thickness of nickel. Exposure tests carried out by the Group, however, emphasize that, as indeed with the normal unsealed finish, good results are dependent on the nickel undercoat being of as sound quality consistent with its thickness as is possible. If bright nickel is applied, the bath must be well maintained so as to ensure a deposit with no more internal stress than is normal with this type of nickel. This wax-sealed finish is giving good service in commercial application.

**Copper + Lacquered Chromium.** A lacquered chromium finish over an undercoat of copper  
(continued in page 22)

\* At the time the investigations were started, the revised Standard B.S. 1224:1953 had not been issued.

# THE INSTITUTE OF VITREOUS ENAMELLERS

## 20th ANNUAL GENERAL MEETING AND CONFERENCE IN MANCHESTER

### Report of Proceedings and Presidential Address

THE ANNUAL general meeting and twentieth annual conference of the Institute was held in Manchester, at the Midland Hotel, on October 7 to 9, 1954. Over 200 members and guests attended, and took part in technical sessions, works visits and social functions.

On the morning of October 7, Mr. A. Biddulph (chairman of council) presided at the annual general meeting. In his report to members he referred to the increasing membership of the Institute, and said that a revision of the Articles of Association had been initiated to bring them into line with current requirements. Two technical sub-committees had presented reports during the year at the Eastbourne Spring Conference and work in the others was proceeding. A recommendation had been made, with the co-operation of Dr. H. W. Webb, O.B.E., for further aspects of one technical matter to be the subject of research in an educational institution. The Summer School at Ashorne Hill had been very much better attended than in the previous year, and a further one would be held in 1955.

Mr. Biddulph reported that the raw-materials sub-committee had been instrumental during the year in facilitating the importation of lithium carbonate, and attempts were being made to reduce the shortage of sodium silicofluoride.

In announcing the 1955 annual conference, which is to be held in Leamington Spa, the chairman emphasized its international character. He then announced the Institute's awards.

The Whittle Medal and prize was awarded to Mr. K. Maskell of Richmond's Gas Stove Co. Ltd., for his paper "Towards Thinner Ground-coats". Mr. E. R. Evans (B.C.I.R.A.) was awarded the Grainger Medal for the best paper presented at an Institute meeting; Mr. Evans' paper was on the blistering of cast-iron enamels and had been presented to the Midland Section of the Institute.

During the meeting the financial report of the Institute was presented by the hon. treasurer, Mr. W. S. Grainger, and was adopted. Mr. Grainger said that the Institute was in a quite healthy position, with a slight excess of income over expenditure, and Mr. Biddulph had stated earlier that it had been decided to try and augment membership rather than to increase subscription rates.

#### Election of Officers

Next came the formal election as president of Sir George Briggs, managing director, Simplex Electric Co. Ltd., who had served as vice-president during the past year. Sir George was unavoidably absent from the meeting owing to illness and coupled with the unanimous vote approving his elevation to the presidency, was a wish for his rapid return to full health. It was announced that the presidential address which Sir George had prepared would be read by Mr. J. W. Gardom, a past-president of the Institute.

The result of the ballot for the election of three members to fill vacancies on the council was next announced, the elected members being Mr. J. Hooper, Mr. T. J. McArthur and Mr. W. Thomas.

Following the reading of the presidential address, which was entitled, "Why Vitreous Enamel", Mr. W. H. F. Tickle gave a talk on "Adhesion".

The afternoon of October 7 was devoted to a Symposium on "Direct Application of Finish-Coat Enamels to Steel" by A. W. Murdoch and B. Zick, and in the evening the annual banquet was held, prior to which the delegates were received by the deputy-president and Mrs. H. Hartley, and the chairman of council and Mrs. A. Biddulph.

On Friday October 8, the morning was devoted



to a Symposium on "New Finishes and Materials—A Challenge to the Vitreous-Enamelling Industry". Mr. J. Hooper introduced the subject and gave the summing-up, while Mr. E. W. B. Dunning gave the consumer viewpoint, Mr. G. Murray outlined practical applications of competitive finishes, and Mr. H. Silman dealt with scientific and technical aspects.

Visits to the works of Ferranti Ltd., and Blake Vitreous Enamelling Ltd., took place during the afternoon, these being followed by an informal

dinner and entertainment at the Midland Hotel in the evening.

The conference concluded on the Saturday morning with a technical session devoted to reports from the technical committee, and to technical queries.

It was announced that although in the future no Spring Conference will be organized, there is to be a works visit to the Steel Co. of Wales Ltd., early in 1955, organized for members on a national basis.

## ★ ★ ★ WHY VITREOUS ENAMEL?

### Presidential Address delivered to the Institute of Vitreous Enamellers by Sir George Briggs

IT IS for me a source of great regret that I am unable to speak to you in person, as I had entertained much pleasure in this prospect, more especially as I feel that, since you have already been well educated in the viewpoints of the gas industry, it is now high time that—to my mind—more pertinent factors of electricity were put before you.

Obviously I would not attempt to expound the merits of the electric as opposed to the gas cooker: there is a place for both. But I am happy to say that whereas the gas industry, by virtue of its greater production, was by far the larger user of vitreous enamel, at long last the electric-cooker industry is overcoming the tremendous set-back it received due to power cuts and restrictions in the use of electricity.

Gas is still in the lead, but I am sure that in asking me to be your president, you recognize that there is another competitor in the field. There are already three million electric cookers in use in this country, and the present annual production rate, based on the first nine months of 1954, exceeds 400,000.

It is clear that the steady increase in the ratio of electric to gas cookers will continue. The significance of our diminishing coal resources and the advent of atomic energy has doubtless occurred to all of you. I should like to emphasize that this is no pipe-dream of the future; the first atomic-energy power station is already under construction, and it is in the foreseeable future that nuclear energy distributed in the form of electricity will provide the greatest form of power in the country. Although it will be some years before it is possible to make extensive use of nuclear power to generate electricity, nevertheless it is now clear that electricity is the only safe and economical means of distributing the great benefits of this wonderful source of energy to every home in the country.

This, however, is merely a background to the future of industry in general, and we need hardly concern ourselves here with the exact share of the cooker market that gas or electricity can expect to obtain for themselves. Having indicated that I am aware that gas cookers exist, I propose to ignore them for the remainder of what I have to say, and concentrate on the interests common to us all.

The significant fact is that more than a million cookers a year will be produced in this country, every one of them requiring a large proportion of its components to be vitreous enamelled. It seems of importance to me that the vitreous-enamelling industry should appreciate the magnitude of the task which lies ahead of it, and take steps immediately to prepare itself. It would be sad indeed if, with the present increasing demand for domestic appliances of all kinds, and a clear road to still higher demand in the future, the enamelling industry should fail to derive the maximum benefit from the greater prosperity which lies within its reach, purely because of its failure to grasp certain elementary, but none the less fundamental, facts.

My choice of title may appear odd, but I have chosen it with a definite purpose in mind. I am seriously concerned about the determined efforts, by many of the present users of the vitreous-enamelling technique, to get away from it because of its unreliability and uncertainty under various conditions. A situation may conceivably arise whereby this great industry might find itself outclassed in the sphere of mass production and merely be used for minor decorative purposes.

It is widely acknowledged that there have been substantial advances in the quality, consistency and characteristics of enamel frits over the last thirty years, and credit is due to the skill and enterprise of those who have evolved them, while

not in any way conceding that the ultimate has been achieved. None the less, all of us here are only too well aware that our house is not entirely in order. Every day we meet with complications both undesired and unforeseen that make clear that the process of vitreous enamelling is fraught with serious problems.

What, in fact, are these problems which at present ham-string the industry?

First, the designer of any product intended for mass production must take into consideration the characteristics of the materials with which he has to work. Whether he is an architect, a cabinet maker or an engineer, an intimate knowledge of the limitations of his materials is essential. While, however, this is a situation common to every industry, and one that must be expected to arise, the designer of a product that is to be vitreous enamelled is restricted by limitations far more stringent than those implicit in the base materials he has to use. No other finish restricts the designer to the same extent as vitreous enamel; indeed, he is often persuaded to subjugate the functional requirements of his product to the processing requirements of vitreous-enamel application. It is not altogether surprising that he looks for alternatives.

Are we sure that this multitude of restrictions on the design of components to be enamelled is unavoidable? Is it not possible that a closer control of frits and application processes—a deeper investigation into the causes of enamelling failures—might lead to the discovery of materials and methods more tolerant of design variations?

If some of the effort expended by enamellers in finding fault with component design was directed towards developing means of supplying the finish, the scope for the use of vitreous enamel would today be increasing, instead of diminishing, as is so sadly the case. The designer who chooses a plastic moulding or a steel pressing protected by plating, painting, or plastic coating, has a far wider field of choice in his approach to the functional requirements of his product than he who is forced to use a vitreous-enamel finish.

It is our duty in this industry, not only to disseminate to designers information on the requirements of economical and successful vitreous enamelling, but also to work constantly towards the improvement of the materials and methods of application, so that designers will welcome vitreous enamel as a finish, rather than avoid it wherever possible.

Second, we find ourselves continually confronted by the appalling need to reject a very high proportion of our products due solely to defects in the enamelling. Statistics have been published recently which lead one to the reluctant conclusion that a reject figure in the neighbourhood of 50

per cent is not unusual. Quite apart from the evident and immediate waste of time and materials, such a situation inevitably has the secondary effect of causing a complete upheaval in the shops concerned, resulting in dislocation of the flow, and the piling-up of unfinished products in such a manner as to detract from the benefits that should be derived from a mass production process.

Third, we come to the disadvantage inherent in the use of vitreous enamel, that is, its brittleness. We have had to accustom ourselves to allowing vitreous-enamelled products a degree of feather bedding which is costly to the producer. This falls very heavily on the electrical industry, which exports the highest proportion of cookers, and adequate protection of vitreous-enamelled cookers for overseas markets results in such a build-up on landed cost that the industry finds itself unable to compete with local products.

At first sight, these may seem separate and unconnected problems, but on closer inspection it will appear that they have one common denominator, namely the effect of all three is increased cost. As you will all know, the paramount feature in a competitive economy is cost, and it is this item that must be given due consideration in all aspects from the raw material to the delivered product. It has been claimed that the cost of vitreous enamelling cast iron has become prohibitive because of difficulties in application, which in themselves are a direct concomitant of a raising of standards and the current demand for self-colour, acid-resisting enamel in pastel shades, and a generally unsatisfactory quality of castings. Similar reasons are produced to explain away the high cost of enamelling sheet steel where a particular trade and quality are specified as essential for satisfactory enamelling. Such specialization inevitably assists in the maintenance of high prices.

This is only one aspect of the situation; increasing labour costs, fuel and freight charges, are constantly tending to force up the price of enamels, castings, and sheet steel, and in view of the advance of competitive finishes, the vitreous-enamelling industry cannot expect to reap any benefit from the increase in overall production unless these problems are adequately solved.

If approached in a new spirit of determination, the difficulties can be resolved. It is unfortunate that it is exactly this spirit which is so lacking. Furthermore, a time-honoured cloak of secrecy appears to persist in certain sections of the industry which results in a pronounced tendency to withhold vital information, and promotes a form of selfish competition. There exists already a fund of technical information, the value of which is appreciated by the more progressive members of the industry, but there are far too many undertakings which cannot be persuaded to modify



their methods in the light of this information. The prevalent thought that they, as individual organizations with years of experience in vitreous enamelling, could not have attained their present status had they not been experts in their trade, is, in general, an attitude more dangerous to themselves as individuals than it is to the industry as a whole. None the less, as is usual where an industry such as vitreous enamelling is made up of so many individual units, the malaise is in danger of spreading to the entire industry.

These then are the problems; to what extent are they being met by the industry today, with solutions that are both realistic and effective?

I have referred to the factors which give rise to the high cost of vitreous enamelling, and must accept that they do exist; none the less, the attempts that have been made to justify this cost would appear to have been accepted in such a manner as to leave one with the uneasy feeling that the main issues are not being tackled with sufficient determination on an international scale. Information is available, but it is of no value unless it is used in conjunction with the correct attitude of mind and respect of first principles that welcome modification and enable industry to keep pace with scientific progress. It seems wrong that a number of us who are vitally interested in vitreous enamelling, are spending much time and money seeking alternative finishes, instead of directing our efforts towards the improvement of existing techniques.

There is much that could be done. We need research into the possibility of evolving new and revolutionary frit mixtures, as well as the possibility of employing different base materials. The techniques of application are becoming outmoded—an alternative should be sought, and fusing methods could well benefit from a reconsideration of the whole process. At the present time our range of finishes is limited; not only might those that exist be improved, but new ones added to our lists. Colour matching is a problem well worthy of consideration, while the utmost effort should be devoted to improve the ability of vitreous enamel to resist mechanical impact.

The results of such research are worthless unless they can be made available to designers at the earliest possible moment, so that traditional limitations to design may be swept away and the improved functional aspects realised without delay.

Two years ago, Dr. Hartley mentioned £100,000 as the figure for production losses which arose in the enamelling departments of the group of companies of which he is chairman. This is a large sum, and such wastage could certainly be partially avoided as a result of much needed research and development, and still further recon-

sideration of production processes throughout the industry. This is the case for closer co-operation between designers and producers; too long have we suffered at the hands of the enamel-shop manager, who says "you can't make it like that". Nor is close collusion within the firm sufficient to our needs. It is not enough that the technicians of one industrial organization attempt to solve the problems in vitreous enamelling only within that organization; it is of prime importance to the survival of the vitreous-enamelling industry that a spirit of co-operation becomes effective within the industry as a whole.

It is with this in mind that the council of this Institute provides special training courses at centres such as Ashorne Hill, where the technique and administration of adequate supervision can be disseminated throughout the industry. This aspect of training of personnel is to be highly commended, for the degree of supervision necessary today is greater than ever, in view of the tendency towards a reduction in individual skills throughout the country as a whole. The training of operatives is a not too difficult task for the skilled and experienced supervisor who fully appreciates the importance of each element in the enamelling process.

To be fully qualified, the supervisor must have some knowledge not only of the means of using his materials, but also of their properties, in order that he may deal with those difficulties which arise during processing, to which no reference is made in the published literature.

At the present time, the Institute arranges visits of supervisors from one factory to another. While the principle is one from which the industry could derive much benefit, the present organization leaves room for improvement. A whole group visiting a factory for an hour or two may derive much personal interest from the trip, but little of lasting value can be obtained in so short a time and under such conditions. Technical papers, conferences, and refresher courses, play a useful role but are not in themselves fully adequate to the purpose.

The dissemination and absorption of relevant information should be a continuous process rather than a spasmodic activity, and should tie in closely with days rather than hours in the appropriate departments in the factories of other members of the industry, such exchange periods being run on an individual rather than a group basis.

It will be objected that this necessarily entails members of the industry finding out what their competitors are doing. This may be so, but it scarcely seems a relevant objection when it is the survival of the whole industry that may depend on just such a publication of achievements both

within and without the industry. Mysticism is out of date; common sense and co-operation are essential.

In what has so far been said, those concerned with the processes of application have been called upon to play a more determined part, but this must also apply to those who supply the raw materials. An attempt must be made, before it is too late, to provide enamels which retain the heat and corrosion-resistant properties of the current product and are, at the same time, less critical in their physical and chemical behaviour. Because of the metallurgical characteristics associated with the heating of metals to within their critical ranges of structural transformation and chemical reaction, it would appear to be of some urgency that a combination of oxides and other metallic salts be found which will make feasible an overall reduction in working temperatures. Not least among the advantages of such enamels is the great economy in fuel consumption which would result from lowering fusing temperatures by, say, 100°C. Moreover, cracking and distortion would be less prevalent, physical and chemical changes less vigorous in their reactions, and the life of furnaces increased. Without prejudice to any of the existing properties of the vitreous enamels that we use, a wider range of fusing temperature is essential so that control may be less critical without any lowering of standards.

The foregoing are essentials, bare bones around which the future of the industry must be built. It is not yet too late to activate this skeleton in order that vitreous enamelling may retain and expand its present prestige. However, this is no moment for complacency.

Two years ago, the Institute was given fair warning of the tendency, consequent upon the inherent difficulties and cost of vitreous enamelling, to move away from cast iron. This forecast is fast becoming reality. The electrical industry has always played a leading part in the creation of standards, and was an early producer of an all-vitreous-enamelled cooker. It is extremely disturbing to observe, however, that it is this very sector of the industry that has now branched out to be the first to take advantage of the new substitutes, in that electric cookers were the first to be offered with non-vitreous-enamelled sides. This is quite obviously a danger signal of the first magnitude.

A part of the time of this Annual Conference is to be devoted to the subject of competitive finishes, so there is no need to enter into a detailed discussion of the subject now. It is perhaps worth just considering the question briefly. Resistance to corrosion and heat are the most important properties of vitreous enamel, brittleness its major disadvantage. There are other materials appearing

on the market which will compete with vitreous enamel on the basis of both heat and corrosion resistance, and sheet steel with a plastic covering is now being used increasingly for domestic products, other than cookers. If I may cite an example, the traditional vitreous-enamel interior surface of refrigerators is at the present time undergoing just such a change.

Where another form of protective covering for ferrous metals is easier and cheaper to apply than vitreous enamel, there can be no argument that will prevent an increase in demand for the one and a decrease in demand for the other. Nor is this the limit: there will be materials which will totally replace the protective covering of metals, as they will be in themselves mechanically, physically and chemically, strong enough to be used in place of enamelled sheet.

With regard to the electric-cooker industry in particular, the flexibility and adaptability of the heating method enables finishes and materials to be used which would not be feasible in cookers heated by alternative means, because of the corrosive by-products of combustion. It is to be expected, therefore, that in the cookers of the immediate future, vitreous enamel will be called for only in actual spillage and cooking areas, and not even there unless the development of enamels and methods of application at least keep pace with the development in competitive materials.

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### Alternatives to Nickel under Chromium Plate

(continued from page 17)

alone has a useful life little more than that of the lacquer. Unpublished work by the British Non-Ferrous Metals Research Association (R.R.A. 1019) has shown that a chromium finish over copper alone rapidly becomes stained on exposure and is then difficult to clean. Poor results may thus be expected from a lacquered finish once the lacquer has been penetrated or has flaked because of corrosive action. Lacquered finishes have served as a stop-gap in the absence of nickel, but their potential future use in any such emergency is clearly dependent on the development of improved lacquers.

**Bronze Undercoats.**—The atmospheric exposure tests carried out by the Group have spotlighted the superiority in corrosion-resistance of a 10-12 per cent. tin bronze deposit, as applied by the proprietary process mentioned, as an undercoat in place of copper. Whether applied with or without a thin deposit of nickel between it and the chromium, the bronze is to be preferred to copper. This finding has been made also by the British Non-Ferrous Metals Research Association.

The Paper here published in an abridged version was presented to the 1st International Conference on Pressure Die Casting, organized recently in London by the Zinc Alloy Die Casters' Association. The review covers both zinc- and aluminium-alloy castings and a full report of the discussion following its presentation is appended.

THE NEED and selection of a surface finish are matters decided by the nature of the component, its function and the conditions which it will meet in service. Many aluminium and zinc-alloy die castings require no applied finish for certain applications, although a finish may be desirable for decoration for protection in particularly adverse conditions or for increased surface hardness for example. Magnesium alloys however, are almost invariably provided with some form of surface finish.

Open atmospheric exposure tests carried out over ten years have shown that zinc-alloy die castings suffer little other than the assumption of a not particularly attractive grey colour. Particular importance is attached to the necessity for avoiding impurities in the zinc alloys in order to ensure good corrosion resistance and ease of finishing.

#### Electrodeposited Finishes

Electrodeposited copper-nickel-chromium coatings are frequently used for the decoration of zinc-alloy die-cast components, the presence of the copper being necessary to prevent heavy local corrosion of the basis alloy at pores in the nickel coating. The copper can only be deposited directly from specially formulated solutions, which are somewhat difficult to operate in commercial practice.

In view of the tendency to porosity in thin nickel deposits and the consequent danger of enhanced corrosion of the underlying zinc alloy a thin deposit of nickel should not be used and every effort should be made to reduce porosity. A thinly applied coating can soon assume an appearance which is worse than the greyness which is developed on an unplated component.

Tests on die-cast zinc-alloy accessories on a number of American motor cars have established that five years' flawless service could be obtained with total thicknesses of plated coatings of be-

## Finishes for Die Castings

By

A.P. FENN\* and

L.A.J. LODDER†

tween 0.0012 and 0.0015 in. in certain American cities.

The use of bronze as an undercoat to chromium, and of single coatings of tin-nickel-alloy plate as measures of nickel economy have met with some success. Great care must be taken to ensure that no castings plated with tin-bearing alloys are permitted to be re-melted for re-use.

During pre-plating cleaning cycles, evolution of hydrogen at the zinc-alloy surface must be kept to a minimum as excessive hydrogen evolution has the effect of considerably accelerating the formation of an alloy layer between the basis metal and the copper deposit.

For some applications chromium up to thicknesses of the order of 0.0002 in. can be applied direct to zinc-alloy die castings as also may brass coatings.

#### Organic Finishes

A wide variety of air-drying and stoving organic finishes is available for use on zinc-alloy castings, the only restriction is that imposed by stoving times and temperatures which must not exceed 30 minutes at 220°C. or three hours at 150°C. In practice this does not constitute a serious limitation.

Zinc surfaces offer a relatively poor key to paint coatings, but sound adhesion can be readily achieved by pretreatment with phosphate or chromate solutions.

#### Chemical Finishes

Most chemical finishes applicable directly to zinc alloy die castings are effected in solutions containing chromate. These produce normally a golden-yellow coloured film which inhibits formation of "white rust" and similar corrosion products. Recently the yellow colour has been bleached by immersion in a mildly alkaline solution to give a clear or slight iridescent film which may be lacquered. This appears to provide a satisfactory solution to the problem of providing polished zinc-alloy die castings with a durable lacquer coating.

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† Imperial Smelting Corporation Ltd.

Black coatings may be produced by immersion in solutions of salts of other metals, *e.g.* copper, nickel and molybdenum. These are not in themselves protective and must normally be lacquered. Black chemical finishes based on chromate coatings have been developed in America and there are also alternative methods based on the absorptive properties of phosphate coatings for stains and oils.

#### Other Finishes

Among the black finishes in commercial use the best prospect of durability appears to be offered by lacquered electrolytic black nickel. Vacuum metallization is of some commercial interest and typical of its application is an instance in which zinc-alloy die castings are phosphated, lacquered, stoved, coated with between 0.000001 and 0.000005 in. of aluminium by vacuum metallization. The coated work is finally lacquered to give good resistance to corrosion.

#### ALUMINIUM-ALLOY DIE CASTINGS

A number of chemical treatments have been developed specifically for the preparation of an aluminium surface for painting. These are normally based on solutions containing phosphates or chromates. The need for the mechanical or chemical pre-treatment of the surface can sometimes be eliminated by the use of wash or etch primers. These primers have a vinyl-resin vehicle pigmented with zinc chromate, to which are added thinners containing phosphoric acid. The primer and thinners are packed separately and when mixed have a useful life of up to eight hours. Application is preferably by spray, but may be brushed and should be allowed to dry out before the application of further paint coats.

Nearly all common types of paint are suitable but those containing salts of copper or mercury or metallic bronze or graphite powder, or in certain conditions, red lead, are not to be recommended, in view of the danger of electro-chemical attack. One of the most satisfactory inhibitors on aluminium is zinc chromate.

#### Electroplated Finishes

Processes for the production of electro-deposited coatings on aluminium are based on the production of a preliminary zinc deposit on properly prepared aluminium surfaces, the zincate immersion process depositing zinc by chemical reaction, whereas the Vogt process makes use of an electric current for this purpose.

Plating techniques require modification for the treatment of different aluminium alloys, particularly casting alloys. Those containing appreciable quantities of silicon or magnesium being less amenable to plating.

#### Anodized Finishes

The production of anodic coatings on aluminium at the present time is principally effected in solutions of either chromic acid, sulphuric acid or oxalic acid. Chromic-acid films tend to be grey and rather opaque. Sulphuric-acid films are transparent and colourless while those produced by the oxalic process, using direct current, are generally light straw colour, and using alternating current vary from brass yellow, through gold to bronze, except in the case of silicon-rich alloys, which remain grey. These finishes must be borne in mind when selecting processes for subsequent dyeing.

#### Hard Coatings

Hard surfaces on aluminium can be produced by hard chromium plating of a thickness not less than 0.001 in. applied direct on most aluminium alloys, but preferably not those containing over seven per cent. magnesium. Recent developments in the U.K. and the U.S.A. have led to the production of hard anodic films up to 0.01 in. thick. These are exceedingly hard with very high resistance to abrasion.

#### Magnesium-alloy Die Castings

Pretreatment for magnesium castings comprises chromate immersion, the subsequent painting procedure being similar to other metals.

Progress in the production of electroplated coatings has only recently been significant. One successful process involves the deposition of a zinc film from a solution which is very different from that used for aluminium. Thereafter copper and nickel etc., can be deposited.

#### DISCUSSION

Mr. A. P. FENN (Birmingham Aluminium Casting (1903) Co. Ltd., in presenting the paper, said that in all finishing of metal, and particularly die castings, the first essential was cleanliness. It was most important that all castings should have the cleanest possible surface if the best results with any finish were to be obtained, and particularly with those finishes which had been dealt with in the paper.

There was a vast number of finishes which could be applied to aluminium alloys. Aluminium die castings as such presented a very useful finish, and for many purposes needed no further finishing after they left the die, apart from fettling and trimming. There were mechanical finishes which gave very pleasing results, and which had been mentioned in the paper; there were paint finishes, with which everybody was very conversant; and there were electroplate finishes on aluminium, which were coming forward very rapidly and with which some very good results were being obtained. The warning should be



given, however, that aluminium had not reached the stage where automatic plating could be employed.

On the question of anodic finishes he felt that a word of warning was also necessary which had not been given in the paper, in that with die castings for decorative purposes there was sometimes difficulty in getting a pleasing result due to flow marks in the casting or certain slight impurities which came to the surface of the casting. Hard surface finishes on aluminium were relatively new, but were being developed very rapidly at present. The hard anodic coating in which the anodized film could be as thick as 0.005 in. could now be satisfactorily produced and direct hard chrome plating on aluminium, particularly for such things as cylinder bores in small petrol engines, was also proving exceedingly satisfactory.

Mr. L. A. J. LODDER (Imperial Smelting Corporation Ltd.), continuing the presentation of the paper said that many zinc-alloy die castings received no surface finish and performed well if unobtrusively in that condition. That was in accordance with the favourable results of atmospheric exposure tests on zinc-alloy die castings, and applied only to castings of adequately high purity. The fact that the general resistance to corrosion of zinc die casting alloys was sometimes questioned was a legacy from the unfortunate days of the earlier zinc alloys. The authors took this opportunity to emphasize the durability and dependability of pure zinc alloys, because of the lingering prejudice which still existed in some quarters.

If account were taken of the fact that chromium plating was by far the most common finish on zinc-alloy die castings, it could be deduced that the majority of such castings were finished for decorative rather than protective purposes. Outdoor exposure constituted about the worst condition which many plated castings had to meet—motor-car accessories, for example—and uncoated zinc alloy was quite satisfactory in this environment. There were two main classes of finish, electroplated and organic, but chemical immersion finishes were of some importance.

In considering plated coatings, the authors had dealt more with their function than with plating technique, and had given some consideration to durability. Nickel had by long experience proved to be the ideal supporting medium for a final chromium deposit. As it had a resistance to corrosion not very different from that of zinc, it might seem curious that the durability of a chromium-plated finish should be dependent on the thickness of the underlying nickel. However nickel and copper coatings would both accelerate the corrosion of zinc alloys at the base of pores,

ultimately causing blisters and serious deterioration of the appearance of the lustrous chromium plating, and therefore a good nickel coating should be employed which was adequate for the service envisaged. In depositing it, the conditions should be such that the coating was of optimum quality.

In the case of organic finishes, emphasis was placed first on the benefits of appropriate pre-treatment. Proprietary phosphate processes had been available for many years, but despite this their advantages were not so widely known as one would wish. Although it was not so universally applicable, chromate treatment had some value in this field and constituted a useful auxiliary defence beneath an organic coating to come into play at points of weakness or deficiency.

There were interesting possibilities in some of the newer types of organic finish which had been made available relatively recently, and increasing experience of their performance might well extend the fields of use of zinc-alloy die castings to more corrosive and hitherto unacceptable environments. Steps in this direction must be taken cautiously, however, because it was obviously dangerous to rely on the physical exclusion of corroding media from susceptible material unless an absolute assurance could be had of the imperviousness of the coating. Multiple coatings of new organic media with specified thickness might permit exploration into the region of some doubtful applications.

Chemical finishes could cover a very large range if those on plated zinc-alloy die castings were taken into account. The authors had discussed them briefly, and mainly with reference to the usefulness of black immersion treatments and the merits of the chromate treatments. They had mentioned several electrolytic black treatments, including black nickel, which was probably the only one of commercial interest.

In conclusion, a process of recent development, vacuum metallizing, was described briefly. Its progress must obviously be watched with interest.

The paper was necessarily incomplete, and there were many omissions, some deliberate and some due to oversight. If delegates could from their own experience fill in the gaps it would serve a useful purpose.

Mr. F. RICHTER (Metallgesellschaft A.G., Frankfurt am Main, Germany) said that one very interesting process had not been mentioned, the so-called Granol process, which was being used now in Germany. In this process small pure aluminium particles in the form of a spray were used in the same way as was used in sandblasting, and this gave a deposit which remained on the castings. After a short period of treatment, the castings had an attractive silvery surface. The pure aluminium protective surface formed on the

castings in that way was not only of decorative value but able to give a very high degree of resistance to corrosion, and this protective layer served to protect the surface against dirt and oil, which was particularly important for motor-car parts such as gear cases and so on. In addition, it made them look very attractive, which from the point of view of sales technique certainly had its advantages.

Mr. W. F. BRYANT (Charles Hill and Co. Ltd., Birmingham) said that the finishing methods used in the U.S.A. were on the whole more efficient than those employed in Great Britain. The Americans considered finishing at the design stage, whereas in England finishing was left to look after itself, with subsequent troubles in production and loss of efficiency. That could be largely overcome by greater co-operation between the caster and the finisher. In the paper references were made to the good corrosion resistance of die castings treated by the vacuum metallizing process, and it was stated that the durability was very good. Mr. Bryant would question that, but perhaps the authors could give some further information on the subject.

Mr. A. W. BRACE (Aluminium Development Association, London) said that under the heading "Anodized Finish" it was indicated that sulphuric-acid anodizing was commonly employed in this country and it was stated that sulphuric-acid films were transparent and colourless in themselves, taking the appearance of the metal on which they were formed. That statement would apply to pure aluminium, but when one was dealing with aluminium die-casting alloys containing large quantities of silicon, he thought that Mr. Fenn would agree that one hardly obtained a clear, transparent film. There were still, Mr. Brace felt, a number of technical problems to solve in connexion with aluminium die castings, and one or two difficulties. They were mainly related to the fact that the alloys which responded well to the pressure die-casting process were ones which contained high percentages of silicon, and that was notorious for introducing difficulties in producing a satisfactory anodized finish, and particularly one which would give good colours, especially in the paler shades. Broadly speaking, it was necessary to effect a compromise by using the lowest silicon and copper content practicable in order to obtain more satisfactory results from anodizing.

There was some indication that aluminium-magnesium alloys might offer a promising line of development particularly when an anodized finish was required, but it was too early to say what the real potentialities of those materials were. He was sure that among users there was a very important potential field of application if

it were possible to produce better quality anodized finishes on pressure die castings, but some problems and a big challenge were presented to the founders, and he did not suggest that it was an easy question by any means.

He would like to draw particular attention to the development of the process which enabled thick, hard, anodic films to be produced with aluminium, including the aluminium casting alloys, because by this means it was possible to treat any small portion of an aluminium die casting to give a surface layer which was comparable in wear resistance to that produced by the case-hardening of steel, which would mean that on many occasions it was cheaper to hard-anodize a portion of a casting rather than use a pressure die-cast insert, which might be more expensive.

He would like to conclude with a brief comment in relation to magnesium alloys. In the U.S.A. two hard-anodizing processes had been developed, one by the Dow Chemical Company and the other by a research laboratory of the U.S.A. Army, which also enabled fairly thick and hard anodic films to be produced on magnesium in the same way as was possible with aluminium. This was a very interesting development, and one which might help to develop still further the use of magnesium-alloy die-castings in more specialized requirements.

Mr. R. W. BAILEY (Zinc Development Association) expressed interest in the remarks made by Mr. Brace on the use of a thick anodized film on aluminium and on magnesium. In the case of zinc, and to a large extent in the past in the case of aluminium, the difficulty with the anodized or chemical dip films had been that the surface of the casting was not sufficiently uniform to overcome the difficulty of crystalline structure in the coating. In the case of zinc there had been, of course, the thin chromate films which were capable of taking dye finishes, but none of these had been very corrosion resistant or abrasion resistant and, although difficulties of light-fastness had been overcome, it could not be said that a satisfactory commercial finish had been developed on the basis of a chemical dip. Work was starting in this country, however, on anodized finishes for zinc and zinc-alloy surfaces, and there seemed to be a promise of the possibility of developing a thick anodized film. It would be interesting if delegates had any news of developments in other parts of Europe which might have some bearing on this work.

Mr. L. J. BRICE (Ministry of Supply, London) said that he had been pleased to hear Mr. Lodder say that if there was any contamination of the basis metal it was not possible to have good protection.

He would draw attention to a point which had



not been emphasized in the paper, namely, that when zinc-base or aluminium-alloy die-castings were being contemplated for specific uses, it was necessary to consider not only their ultimate environment and means of protection against it, but also the important question of any inter-metallic contact which the finished component would have.

Apart from the specific protection of individual components, it was important to consider the question of packaging. In some industries castings might go almost straight from the die caster to the user, but in other spheres there were quite considerable waiting periods, which might be in different climates, and so the question of efficient packing methods had to be considered alongside that of actual protective measures for the components themselves.

Finally, he would like to ask whether a little more information could be given, perhaps by technical references, to the vacuum metallizing process which so far as he was concerned was quite a new technique.

Mr. F. RICHTER said that, in his experience, aluminium pressure-die-castings could only be anodized satisfactorily for corrosion-protection purposes. He would like to ask whether in England aluminium castings could be anodized in such a way that they were improved for decorative purposes, or whether it was only for protection against corrosion.

Mr. L. A. J. LODDER, replying to the discussion, said that Mr. Richter had been dealing with metal spraying. The authors had examined this in relation to aluminium coatings on zinc-alloy die castings and had found that the degree of protection, at any rate as judged by accelerated tests, was not too good. Metal-sprayed coatings were, of course, porous by nature and it was a little illogical to put an aluminium coating on a zinc or zinc-alloy surface because, except perhaps in alkaline conditions, zinc was the corroded member.

Mr. Bryant had spoken of design in relation to finishing, and that point, in view of the complexity possible with die casting, required the utmost emphasis. Some account of zinc-alloy die castings in particular was taken in the current British Standard for thicknesses of plated coatings, where a ball of 1-inch diameter was used to exclude certain areas of the surface from the specified thickness standard. In other words, account was taken of the fact that it might be difficult everywhere on significant surfaces to achieve the specified minimum. To his mind, that was the wrong way round, and it would be most desirable, if a good standard of durability was to be maintained, to have the surface in such a configuration that the minimum standard could

be achieved everywhere, so far as possible. The question of design came into polishing, accessibility and so on.

Vacuum metallizing had been referred to by Mr. Bryant and by Mr. Brice. The process was quite a new one, and had only just come into commercial development through improvements in pumping devices, vacuum chambers and so on. There was a short reference to it in the paper, and there were others in the literature, but the one given mentioned the application of the process to zinc-alloy die castings.

Mr. Brice had also raised the question of contacts between dissimilar metals. There it was logical where possible to plate the offending member with zinc. It had been found in the case of castings carrying brass inserts that to chromate-treat the entire component was quite effective, and that applied not only to cast-in inserts but to those put in afterwards. If one examined a chromate-treated casting carrying an untreated brass insert, as against a chromate-treated component *i.e.* casting with inset, a considerable difference would be found in their performance.

On the question of packaging, if damp conditions were met in storage it would be found that chromate-treatment was most effective. Sodium benzoate had come into prominence a few years ago, primarily for protecting steel. Wrapping paper could be impregnated with this compound and would then protect steel very well in damp conditions. This wrapping paper was freely available, and it had some value for zinc where it was possible to get reasonably intimate contact between the wrapping paper and the zinc surface. It might be of some benefit for die castings, although in that case intimate contact might be more difficult to obtain. Absolute contact, however, was not necessary.

The authors had mentioned gaps in their paper. There had been considerable German experience in the field of chemical finishes, and possibly the German delegates could provide some information about that, in particular on the point which Mr. Bailey had already raised of anodized finishes for zinc-alloy die castings.

Mr. A. P. FENN, who also replied to the discussion, said that Mr. Bryant had asked a direct question about the vacuum deposition of metal, and Mr. Brice had also referred to this subject. From such experience as he had had, the deposited metal required definite protection, either by lacquer or in some cases by sealing in a small chamber, such as was done for motor-car headlamps, where the reflector was produced by the vacuum-deposition method and immediately sealed into the lamp to protect it from the outside atmosphere and moisture. Mr. Richter had also referred to a sprayed-metal process.

In answer to Mr. Richter's question about the protective and decorative value of anodizing, it should be pointed out that there were two processes. One of them would provide a thin, very porous film which would satisfactorily take a large amount of dyestuff to provide the beautiful colours which could be obtained on various aluminium alloys, but those colours and that anodic film were not highly protective for aluminium. If it were desired to obtain both results, a thicker anodic film must be given. This could be dyed, but it would not give so pleasing an effect with the very fine pastel shades as would the thinner film. The two processes varied in time and in temperature. To get the best dyed film, the temperature of the bath should be raised a few degrees, which would give a more porous film which would absorb a greater amount of dyestuff, but then there would be less of the protective film present. In the other case the temperature of the anodic bath was kept low, producing a thicker closer film, which would give, however, useful dyeing qualities, particularly for the darker colours.

Mr. Brace had questioned the statement that the anodic film from the sulphuric-acid bath was a clear film, and instanced the anodizing by the sulphuric-acid process of high-silicon alloys. Mr. Fenn however still claimed that the anodic film by the sulphuric-acid process was a clear film. A careful analysis under the microscope would show that it was a clear film, but that the etching of the metal surface before the film was deposited gave the dirty grey colour to which Mr. Brace had objected. There was still, however, a clear film on the top of that. That was why very dark dye-stuffs could be got into that film and hide the grey matter behind. Mr. Fenn was sure that many of those present would agree with him that they were not all working with high-silicon alloys for pressure die castings. Many of them were endeavouring and succeeding in getting away from the high-silicon alloys to the much lower silicon contents possible with other alloying constituents, and obtaining better quality castings, better surface finishes and a better product all round.

The aluminium-8 per cent magnesium alloy which had been mentioned was coming to the fore very rapidly for many parts which had to be supplied for finishing by polishing processes for refrigerators, gas cookers and similar articles. Where it was desired to have a nice polished finish, or a silver finish, very good results could be obtained with this aluminium-magnesium alloy, which was also exceedingly interesting for further anodic finishes. However hard one tried, it was not always possible to get away from flow marks on the surface of the casting, which tended to

spoil the appearance after the casting had been anodized.

Mr. Brice mentioned the question of the contact of dissimilar metals, and that raised a point which Mr. Fenn thought should be emphasized in connection with electroplating, in particular in regard to aluminium and magnesium, although it referred to all the metals. One put on by an electrodeposition process these dissimilar metals, and if the dissimilar metals which were plated on to the parent metal were not good films, without a series of pinholes, one could run into trouble for the simple reason that corrosion of the parent metal would be accelerated by the presence of those deposited coatings of other materials. One regularly saw in the streets the bumpers of motor cars showing rust through the plating. That was solely due, in his opinion, to the fact that the electrodeposited coatings of metal on the parent metal did not form a complete envelope, and therefore allowed moisture to get in, so that electrolytic or galvanic corrosion was set up locally.

Mr. Brace's last point concerned hard anodic films. Mr. Fenn agreed that these hard anodic films could be made and were being made very serviceable, but he would give the warning that where the hard anodic film on aluminium was used as a bearing, or where friction came in at all, arrangements must be made to see that those surfaces were adequately lubricated, or one might run into trouble and find that the film wore very badly.

Mr. F. RICHTER apologized for speaking again, but said he thought that his earlier remarks had been misunderstood, possibly due to difficulties of interpretation where technical terms were involved. The metal-spraying process which he had mentioned was not a process in which a spray gun was used to apply the metal to the surface. What they did was to use very finely powdered aluminium which filled in all the cavities and pores. This aluminium powder was applied by compressed air or a centrifuge to the metal surface. The impact of the aluminium was such that a very fine layer of aluminium was left as a deposit on the metal surface. That was quite different from metal spraying by means of a spray gun.

Mr. A. P. FENN asked whether, after the metal powder had been blown or thrown on to the article, any form of heat treatment of the finished article was given to hold the particles in position.

Mr. F. RICHTER replied that no further treatment was necessary. The result was not as decorative as an electroplated finish, but the casting, the surface of which was not always very clean because of the casting process, was given a homogeneous and even layer in appearance.

# DIRECT

## application of FINISH-COAT VITREOUS ENAMELS to

*Papers presented to a Symposium on "Direct Application" during the Annual Conference of the Institute of Vitreous Enamellers held in Manchester on October 7, 8 and 9, 1954.*

## Sheet Steel

The present position with regard to the subject is dealt with in two complementary papers.

The first paper deals briefly with the development of enamels over the past thirty years, and shows how this has contributed to a reduction in the thickness of enamel coatings which has made possible the direct application of finish-coat enamels to steel. The present-day applications of these enamelling processes are discussed, and special mention is made of metal preparation.

The second paper covers in detail commercial enamelling processes directly on to steel, particular reference being made to titanium steel and specially prepared enamelling steel.

## GENERAL CONSIDERATIONS

By A. W. MURDOCH\*

FOR many years the enamelling industry has been tending towards a reduction in the thickness of the enamel coating comparable with the coverage and finish required. Progress in this direction has been rapid during the last ten years, and has reached the point when enamelling on steel may be entering a new era.

A brief reference to the development of enamels over the past thirty years will assist in tracing the progress which has been made in reducing the thickness of enamel coatings during the same period. Until the middle 1920's the weakly opaque fluorine- or gas-opacified enamels, requiring substantial mill additions of opacifier, were in use, and application weights were in the region of 100 gm. dry weight of white covercoat enamel per square foot of steel area.

From 1925 onwards commercial enamels opacified with antimony in the melt were developed and improved until in the late 1930's the white covercoat application weight for two coats of enamel had been reduced to 66 gm. dry weight per square foot. At the same time the mill addition

opacifier was decreased to 3 to 5 per cent, although the covering power was greatly improved.

In 1939 new types of enamel became available and made a major contribution to the campaign for thinner enamel coatings. These were the zirconium-opacified enamels, and in a few years, development was sufficiently rapid to allow one coat of white enamel to be applied at 40 gm. dry weight per square foot, and produce covering power and whiteness at least equal to two coats of the antimony-type enamels.

Thus it can be seen that over this period of some fifteen years the thickness of enamel covercoat application had been reduced some 60 per cent with a tremendous saving in manufacturing costs and greater resistance of the enamelled surface to mechanical damage. The enameller contributed much to this advancement in the way of application techniques and handling, for each new enamel development requires consideration from the practical enamelling point of view. In the early 1940's an entirely new class of enamels, which had been the subject of experiment for some time, was receiving considerable attention in the laboratory and pilot plant. These were the self-opacifying titanium-base enamels which, as is now well known, have exceptional qualities of coverage and whiteness. By 1946 titanium enamels were commercial propositions, and a new field lay open to the enameller. There was still an enormous amount of development work to be carried out, and this has progressed to the present day when a high degree of coverage can be obtained with 20 to 25 gm. dry weight per square foot of white covercoat. This is approximately one-half the application weight of the zirconium enamels, one-third the amount of antimony enamels and a saving of some 75 per cent on the enamels which were in use thirty years ago.

Besides this, titanium enamels have been produced which will fuse on to steel at a temperature as low as 760° C., and which have a high degree of fluidity during the fusing stage.

It is these latest developments which have brought so much nearer the dream of every

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enameller—the elimination of the cobalt-nickel groundcoat. Any further decrease in the total enamel application thickness by reduction of the covercoat thickness would not appear to be an easy proposition when 0.004 to 0.005 in. of white titanium finish coat can satisfactorily be used over groundcoat to-day. Therefore the elimination of the orthodox groundcoat would appear to be the next logical step.

There has been a considerable amount of work conducted towards this end, and the idea in itself is not new. It has been possible to obtain laboratory samples in one-coat white directly on to enamelling steel for a long time past, but in production certain difficulties were always present, such as the correct quality of steel, the care necessary in its fabrication to avoid scratches and the minimum of metal finishing. These points allied to the problem of adherence have in the past been deterrents to the one-finish-coat on steel programme.

However, there are so many advantages to be obtained from its use that within the last two or three years large-scale research operations have been conducted towards this end. Results have been most encouraging and the goal is considerably nearer, but it would appear that there is still more experimental work to be done before this achievement can become common practice.

So far in this paper only enamelling-stock mild steel has been considered, but specially prepared mild steels and special steels have also received consideration with varying degrees of success and these will be reviewed later. However, enamellers have emphasized that if the process is to be economical the one-coat-white finish must be able to be applied to normal enamelling steel, or at least to a steel which is comparable in cost.

Certain types of direct-on-steel finishes have been in regular production for some time, and are well known, but it is intended to mention such finishes briefly in order that the survey of this class of enamelling may be complete.

(a) *Coloured Enamels.*—In this particular class are the regular groundcoats which may be used for protection of the metal from corrosion on some non-decorative items where the appearance of the finish is not of prime importance. Certain of these groundcoats with the addition of colouring oxides at the mill will also produce a fair surface finish for some articles.

Special dark-coloured frits which have been developed from the groundcoat frits give an improved surface finish and a wider range of colours such as browns, greens, blues and certain tints of grey. Mill addition "A" in Table I is typical for these types of enamels.

In the case of these enamels a regular pickling cycle gives completely satisfactory results, but

nickel dip in conjunction with regular pickle is recommended for the most recent enamels developed in this class which give more brilliant colours than their predecessors. These self-coloured enamels are prepared according to mill addition "B" (Table I.).

A similar metal preparation applies to enamels for lighter colours which have been obtained by the omission of all colouring oxides from the frit formulæ. These may sometimes be used by blending with a soft orthodox groundcoat, and opacifier and colour can be added at the mill as shown in mill additions "C" and "D". In most cases these enamels are applicable to parts where colour is an essential factor, but where resistance to atmosphere or corrosive action is not encountered.

(b) *Self-mottling Groundcoat.*—This is a familiar feature in many enamel shops today, and with the correct frit combinations a very pleasing finish with a high degree of resistance to acid attack can be obtained.

The white mottle is produced by the addition of a suitable titanium frit which may be ground in with the acid-resisting groundcoat frits, or it may be ground separately and mixed at a later stage. A variety of effects may be produced depending upon

TABLE I

|                                      | A   | B   | C   | D     |
|--------------------------------------|-----|-----|-----|-------|
| Groundcoat or dark-coloured frit ... | 100 | —   | —   | 10-25 |
| Self-coloured frit ...               | —   | 100 | —   | —     |
| Frit for light colours ...           | —   | —   | 100 | 75-90 |
| Clay ...                             | 6   | 6   | 6   | 6     |
| Magnesium carbonate ...              | 3/8 | 3/8 | 3/8 | 3/8   |
| Opacifier ...                        | —   | —   | 2-4 | 0-3   |
| Colouring oxide ...                  | 0-5 | 0-3 | 2-4 | 2-4   |
| Water ...                            | 45  | 45  | 45  | 45    |

Fineness: 2 to 3 gm./200 mesh/50 ml. Application: 25 gm./sq. ft. dry weight. Firing temperature: A and B, 820 to 840° C.; C and D, 790 to 810° C.

the grinding fineness and how the mottling enamel is added.

Certain colouring oxides may be added at the mill resulting in attractive finishes, and self-coloured titanium enamels may be used in place of the white. A typical mill addition is given below.

The density of the mottle will depend upon the percentage of titanium enamels present, and this will also control the adherence properties. It is, therefore, recommended that nickel dip be used in conjunction with this finish.

|                        |               |
|------------------------|---------------|
| Groundcoat frit ...    | 50 to 80      |
| Titanium frit ...      | 50 to 20      |
| Clay ...               | 6             |
| Borax ...              | $\frac{1}{4}$ |
| Magnesium carbonate... | $\frac{1}{4}$ |
| Colouring oxide ...    | 0 to 3        |



|                        |     |  |
|------------------------|-----|--|
| Water ...              | ... | 45   |
| Fineness ...           | ... | 2 to 3 gm./200 mesh/<br>50 ml. (This may be<br>varied to suit) |
| Application ...        | ... | Generally 25 gm. dry<br>weight/sq. ft.                         |
| Firing temperature ... | ... | 820 to 830° C.   |

(c) *Over-sprayed Finish.*—This is a further application of the mottled finish mentioned above, which although a two-coat application, is completed in one fire. A thin spray of cobalt/nickel groundcoat is applied to the face side of the sheet at approximately 4 gm. wet weight per square foot, and a regular coating on the reverse side. Then a mixture of groundcoat and titanium enamel is oversprayed on to the wet groundcoat at approximately 25 gm. dry weight per square foot. Fairly satisfactory results are produced where a mottled finish is acceptable.

In this case no special pickling procedure is necessary and adaptations of this have been made by applying the groundcoat thicker and overspraying with an alkali-resisting enamel, as in the case of washing-machine tubs, with or without a mottle.

It is known that at least one plant in the United States has also carried this process a step further and are experimenting with the application of white- and pastel-coloured titanium covercoats as oversprays on to a thin wet coating of regular groundcoat. The finish in white could not be considered first class at the present time, but the off-white finish is of good appearance and no doubt further improvement will be made. The enamels seen in use were not in the low firing class, and it is possible that a 780 to 800°C. firing range would give better results.

(d) *Titanium Steel.*—In 1945 in the United States the first trials of applying white directly on to titanium steel were conducted. The results showed then that there were distinct possibilities of using this material as a base for covercoat enamel in order to reduce the application thickness by the elimination of the groundcoat. There was, however, a considerable amount of work still to be done with regard to metal fabrication and preparation, and also the production of a titanium enamel which had the correct fluidity and fusibility in order to give a glass-smooth surface.

During the next three years enamels and techniques were developed which by 1948 prompted one firm to go ahead with production trials on cooker tops, and since then progress has been maintained.

Enquiry has shown that today much more enamelling on titanium steel would be carried out in the United States if it were in greater supply, and this, in spite of the higher metal cost over

regular enamelling steel, showing that with good shop practice some slight saving in enamelling costs can be realized over the regular enamelling-iron plus groundcoat finish. (A later paper on this subject will deal with plant processing and the economics of using titanium steel.)

It is necessary to use a nickel dip in the pickling process but otherwise procedure is similar to that for regular steel. Opinion varies as to the time of immersion in the hot sulphuric-acid tank. Some operators believe that a rather longer time in the acid is beneficial while others prefer to pass through the acid tanks with as little pickling as possible after a very thorough cleaning. The adherence results in practice will no doubt determine the best procedure for any individual plant.

There is general agreement, however, with regard to the nickel deposition in that a minimum of 0.08 gm. per sq. ft. is essential for good adherence, and that it should be uniform over the steel surface. Maximum working limits do show some variation, from 0.10 to 0.12 gm. of nickel per square foot of steel surface being the agreed average, although some trials have shown that even twice this amount is not detrimental to the adherence properties. Again much may depend upon the type of work and the class of enamel being used.

A typical mill addition for use with titanium steels is:—

|                         |     |                                  |
|-------------------------|-----|----------------------------------|
| Titanium frit ...       | ... | 100                              |
| Clay ...                | ... | 2½                               |
| Bentonite ...           | ... | ½                                |
| Sodium aluminate ...    | ... | ¼                                |
| Potassium carbonate ... | ... | ¼                                |
| Gum tragacanth ...      | ... | 1/16                             |
| Water ...               | ... | 40                               |
| Urea ...                | ... | 1/8                              |
| Fineness ...            | ... | 1 to 2 gm./200 mesh/<br>50 ml.   |
| Application ...         | ... | 30 gm. dry weight<br>per sq. ft. |
| Firing temperature ...  | ... | 820 to 830°C.                    |

(e) *Special Enamelling Steels.*—Certain members of the steel industry have been reluctant to adopt the titanium-killed steel technique due no doubt to the high costs involved and also the special handling required to produce smooth sheets free from scratch marks. They have concentrated on other metallurgical techniques in an attempt to produce a non-boiling steel which could be enamelled successfully with covercoat enamels without the use of a groundcoat.

Small production quantities have been available with varying degrees of success. Some of these special steels received a plating of the surface before being sent to the enameller, but at the present stage they are not considered to be

entirely satisfactory for direct-on enamelling with titanium enamels. Further development by the steel companies concerned will no doubt improve these steels which could be of considerable benefit to the enamelling industry.

Pickling procedure for these special steels employs the use of the nickel tank, and although many variations to standard practice have been adopted the inconsistent enamelling results show that this section is not yet ready for production trials.

(f) *Special Preparation of Enamelling Steel.*—In the paper which E. M. Hommel presented to the I.V.E. Annual Conference in October, 1953, he discussed the application of white enamel directly to steel and the preparation of the metal prior to enamelling. It would appear that only one of these processes is in use at the present time. This is the Ferro-Republic pickling process, and although there is only one plant in the United States which is in production with this process, modifications are continuing to be made and plant trials are showing great promise for its extended use in the future.

The Ferro-Republic direct application process is a metal-treatment process, which permits the application of a wide variety of commercial finish coats to steel. No special enamel compositions or special mill addition materials are required, although preference might be expressed for the lower-fusing titanium enamels at present in use. The metal treatment is carried out in the enamelling plant in conjunction with metal cleaning and pickling; however, several steps are performed which require additional equipment to that normally employed in regular pickling layouts.

The process is applicable to all mild steels but it has the same limitations, and is subject to the same variations in steel quality as conventional enamelling processes. Therefore, at the present time it is recommended that only enamelling iron be used.

There are two essential steps in the process beyond those required for the correct cleaning of the metal. These are the necessity to obtain a deep etch on the ware, which is accomplished by pickling in nitric acid, and the nickel deposition wherein nickel is deposited by chemical reduction rather than by galvanic displacement as in normal nickel-dip practice. This latter practice ensures a more continuous nickel layer than can be obtained by galvanic means. There is additional rinsing necessary but the above two steps are the essential ones, and rigorous control of these cannot be over-emphasized. Details of the solutions and procedure used in practice will be given in a later paper but it will be helpful now to give a little more information regarding the essential features of the process.

With continued use of the nitric-acid pickling bath, the acid concentration will naturally decrease, and a recommended means of controlling the bath is to determine the loss of weight which occurs from a standard size test-piece which is immersed for a definite time in the bath. This specimen should be representative of the metal stock being used. A 4-in.  $\times$  6-in. plate is generally satisfactory with a period of immersion of 45 seconds. At the end of this time the test-piece is rinsed in running water, dried with a towel using a blotting action and finally in a drying oven. Weighing before and after the immersion will give a loss-in-weight figure which is calculated to loss in weight per unit surface area. The weight loss should lie between 4 to 6 gm. per square foot of surface. When the weight loss is approximately 4 gm. per square foot of surface more acid should be added up to the original 20 per cent nitric-acid strength but not above. It is recommended that if the desired loss of weight is not obtained in the specified time then an extension of the time of immersion is desirable rather than increasing the acid concentration further.

This check should be conducted regularly as control routine, and it is absolutely necessary to apply this test before changing from one enamelling steel to another in order to obtain consistently good results. It should be remembered that the nitric acid is used to give a uniform deep etch to the metal, and as various grades and qualities of steel will react differently in this connexion, a control, such as that given above, is essential.

The nitric-acid bath will usually give satisfactory results until the iron concentration exceeds 50 gm. per litre of solution and then it should be discarded.

In the Ferro-Republic process the nickel deposition, as previously stated, occurs by chemical reduction rather than by galvanic action, and it is determined primarily by the concentration of sodium hypophosphite (the reducing agent) and the temperature of the bath.

The reduction of nickel, at the material concentrations and temperatures of the bath, occurs only in the presence of certain metals which catalyze the reaction. Iron is one of these metals and hence it lends itself readily to nickel plating by this method. Under conditions of high concentrations of sodium hypophosphite ( $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ ) and high temperatures the reduction reaction proceeds spontaneously, and precipitation of metallic nickel occurs throughout the solution. The precipitated nickel catalyzes the reaction with the result that deposition continues at a rapid rate until the reacting materials are exhausted. It is important therefore that the temperature of the bath be maintained below the range where the reaction proceeds spontaneously.

The operating temperature is, therefore, arbitrarily set at 130° F. (54° C.) and the reducing agent, sodium hypophosphite, at 0.4 oz. per gallon. Under these conditions with a pH of 3.5 to 5.5 approximately 0.15 gm. of nickel per square foot of surface will be deposited in five minutes on metal prepared in nitric acid in the manner described.

The optimum nickel deposit is considered to be 0.1 to 0.2 gm. per square foot of surface.

The nickel concentration of the bath is not critical, but it should be periodically determined and adjusted to maintain a concentration of 4 oz. of nickel sulphate per gallon of solution.

Sodium acetate acts as a buffer to aid in maintaining correct pH conditions. It requires no control and need not be replenished.

Control of the nickel deposit is by direct determination of the amount of nickel deposited under the established conditions of temperature, pH and immersion time. A test-piece which has been pickled in nitric acid to the point of correct iron removal is plated and the nickel deposit determined by analysis.

To maintain the concentration of sodium hypophosphite an addition may be made after processing a unit quantity of ware. The appropriate amount can be found by experiment.

The bond obtained by this process is excellent,

and the quality generally shows a great improvement over the results which were being obtained less than a year ago. However, the tendency appears to be to use two coats of titanium enamel for the better-class ware. The first coat acts as a white groundcoat, and for this purpose spray-booth scrapings may be utilized giving a highly acid-resistant coating completely through the enamel layer.

Titanium enamels for use directly on to steel include a minimum amount of clay in the mill addition in order to obtain the maximum amount of flow during fusion. A typical mill addition is similar to that given in section (d) with preference for the lower fusing temperature enamels. Extensive trials have shown that the best results direct-on steel are generally obtained if for the same firing time the temperature is some 20° C. higher than that usually used for the same enamel applied over a groundcoat.

In conclusion it would appear that there is still a great deal of experimental work to be done before high-class enamel finishes can be obtained with one coat of white applied directly on to the recognized enamelling steel.

The best proposition so far, apart from the use of a titanium steel, is the two coats of titanium white in two fires applied in conjunction with the Ferro-Republic pickling process.

## ★ ★ ★ SHOP PRACTICE

By B. ZICK\*

THERE are at the moment two commercially accepted methods for obtaining a direct-on-steel white-enamel finish. The first is the use of a special titanium-killed steel, while the other is a special method of preparation for normal enamelling iron. It is intended to discuss in detail current shop practice for both of these methods.

### Enamelling on Titanium-killed Steel

A very impressive production record has been achieved during the post-war years by the one American plant known to be using the direct-on-steel process employing titanium steel.

With regard to fabrication, modification to tools and technique is necessary owing to the greater springiness of the titanium steel. Metal finishing must be kept to a minimum as grinding away or polishing of the metal surface tends to destroy adherence. Deep surface scratches must be avoided at all costs as these will not be covered in the enamelling process.

The metal preparation prior to enamelling follows more or less normal lines, and can be described as follows:—

1. Parts are thoroughly cleaned in a degreaser. It is essential that the steel be completely free of grease, oil and shop dirt prior to acid pickling.

2. In the production pickling process the cleaner is followed by a rinse.

3. Rinsing is followed by a hot sulphuric-acid pickle. The acid solution strength is 6 to 8 per cent, and the temperature 150° F. for an immersion time of 4 minutes.

4. The next step is a cold rinse. The rinse tank is made up with sulphuric acid to give a pH value of 3.0 to 3.5. Immersion in the rinse is for approximately ½ minute.

5. The nickel tank which follows this rinse is made up as follows:—

|                   |     |  |
|-------------------|-----|--|
| Solution strength | ... | 1.3 to 1.5 per cent nickel sulphate  |
| pH value          | ... | 3.2 to 3.5. The pH is controlled by adding sulphuric acid or flake caustic |
| ...               | ... | ...  |

Temperature ... 170° F.

Time of immersion ... 5 minutes

The nickel solution is maintained in the con-

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ventional manner and continuous filtration is employed.

6. Following the nickel is a second acid rinse. This is a sulphuric-acid solution at a concentration of 0.15 to 0.20 per cent operating at a temperature of 90° F. Immersion time in this tank is for approximately  $\frac{1}{2}$  minute.

7. This is followed by two neutralizer steps:

Neutralizer 1—

|                       |  |
|-----------------------|--|
| Solution strength ... | Sodium hydroxide                         |
|                       | 0.2 to 0.4 oz. per gal.                  |
|                       | Sodium cyanide 0.28 to 0.56 oz. per gal. |

|                           |                |
|---------------------------|----------------|
| Operating temperature ... | 130 to 140° F. |
|---------------------------|----------------|

|                    |           |
|--------------------|-----------|
| Immersion time ... | 3 minutes |
|--------------------|-----------|

Neutralizer 2.—This is a borax solution equivalent in concentration to 0.05 to 0.08 per cent sodium oxide.

|                |                |
|----------------|----------------|
| Temperature... | 130 to 140° F. |
|----------------|----------------|

|                    |            |
|--------------------|------------|
| Immersion time ... | 1½ minutes |
|--------------------|------------|

The reason for the use of a second neutralizer is to reduce the tendency of the metal to straining from the effects of the first neutralizing solution and any iron and nickel salts which may be carried over.

The plant enamelling titanium steel uses a continuous pickling machine. The solutions are identical with those used for conventional enamelling iron. It is normal practice to pickle titanium steel and regular enamelling iron together. The acid pickling step is approximately 50 per cent longer in time than on a similar continuous pickling plant using identical solutions where only enamelling steel is pickled. This increased time cycle is to cater for the titanium steel and it appears to have no detrimental effect upon the particular enamelling iron in use which is also given the extended pickle. The reason put forward for this lengthened cycle is the need for a deeper etch than is normally required where a groundcoat is used. Nickel deposition is also increased from the normal 0.02 to 0.03 gm. per sq. ft. to 0.1 to 0.15 gm. per sq. ft., the optimum being 0.12 gm. per sq. ft.

At the completion of the pickling and nickel-dip cycle the steel must be clean and completely free from all trace of smudge. Very stringent control and absolute cleanliness are essential if freedom from crawling and good adherence are to be obtained. Handling after pickling is kept to a minimum in order to avoid finger marking which can cause discoloration to the fired enamel, crawling, or poor adherence.

After pickling, parts are sprayed as quickly as possible. Spraying is carried out in a conventional spray booth, and the enamel used is a regular titanium white. The backs of articles are

only very lightly dusted while a full coat of 30 to 35 gm. per sq. ft. is applied on the face side. This application gives a fired thickness of approximately 0.006 in.

When coated, work is dried and fired in the usual manner. It has been found, however, that firing temperatures for direct-on application have to be raised by 10 to 20° C. to obtain the best results.

The aim is to produce one-coat work, and it is claimed that a satisfactory finish in one coat is achieved on 60 per cent of the work processed by this method.

Components requiring recoating are resprayed after conventional rectification. In the case of crawling the enamel which is rolled back and thickened is stoned down with a minimum of disturbance to the already oxidized exposed metal surface. A local repair is carried out before respraying the whole area. The weight of application on recoat is approximately 10 gm. per sq. ft. Parts can be recoated up to three times, giving a maximum of four coats of enamel. The maximum thickness limit allowed is 0.012 in. Any part which is not satisfactory after the fourth coating and which has the 0.012-in. limit of enamel thickness is stripped by sandblasting. Stripped parts are returned to the spray line immediately without any further pickling or nickel-dip operation, and on reprocessing the adherence is said to be at least equivalent to that obtained on pickled and nickel-dipped ware. Likewise the absence of nickel is apparently not detrimental to the finish. One-coat work on titanium steel compares favourably with a conventional one-coat-white over groundcoat finish, while in the case of a multi-coated article the finish appears superior.

Adherence is checked by the torsion test in conjunction with the normal impact test, as the latter test alone is not conclusive on this type of coating.

Defects encountered in this process are very similar to defects in cast-iron enamelling. There are two types of boiling. The first is caused by under-firing over thick lugs or double thicknesses of material, and the second is a boil which comes from improper cleaning or wiping of the pieces before spraying.

Good welding practice is essential for satisfactory application of covercoat enamel directly to the steel. Electric-arc welding, including spot welding, gives good results, and for gas welding a filler rod of the parent metal must be used. Unsatisfactory welds may cause blistering or "popping-off" of the enamel.

The chief advantages of the process may be summarized thus:—

1. Improved appearance is obtained in as much as (a) there is practically no tendency for the



enamel to sag or slip on repeated firing, and (b) in two or more coats the surface produced is almost completely free of the minute undulation generally associated with a covercoat - over - groundcoat finish.

2. Resistance to chippage and torsional damage is greatly increased. Damaged areas resulting from impact are much reduced in size, being a crushing of the glass rather than an actual flake chipping off.

3. The higher sag resistance of the titanium steel makes the use of a lighter gauge possible together with a reduction in reinforcing and bracing.

In the one plant employing this process on a limited range of components at the moment, it is intended to expand the use of titanium steel as soon as adequate supplies are available.

There are disadvantages of this process such as the extreme care necessary throughout metal storage and fabrication, and the need for precise control in the metal preparation and enamelling processes. Apart from this titanium steel is in very limited supply. In the United States where one steel company is manufacturing this material the cost is approximately 40 dollars (£14) a ton more than that of ordinary enamelling steel. No commercial quantity of titanium steel has yet been produced by a steel company in the United Kingdom.

### The Ferro-Republic Process

The second of the two accepted methods for obtaining a direct-on-steel white enamel finish is known as the Ferro-Republic process. This is essentially a special metal preparation whereby finish-coat enamel may be applied directly to conventional enamelling iron.

At the time of writing, the Ferro-Republic process might fairly be said to be in the pilot plant stage of development, although one firm has been using the process for a special product for some two years. The process consists of two essential steps beyond those required for normal pickling. These are:—

1. The production of a deep etch on the metal surface.

2. A nickel deposition step wherein nickel is deposited by chemical reduction rather than galvanic displacement as in conventional nickel dip practice.

The original process in detail is as follows:—

1. Degreasing and cleaning operation.

2. Sulphuric-acid pickle.—This is a usual type of sulphuric-acid bath, i.e. 6 to 8 per cent sulphuric-acid solution operating at 150 to 160° F. Immersion time is approximately 10 minutes but sufficient time must be allowed to remove all rust and scale.

3. Slightly acid rinse used cold. This is approximately a 0.15 per cent solution of sulphuric acid by volume.

4. Nitric-acid pickle.—This consists of a 20 per cent solution (by volume) of nitric acid operated at room temperature. Immersion times vary from 20 seconds to one minute depending on the pickling behaviour of the steel. As the bath is used the acid concentration decreases, and it is necessary to add nitric acid to bring the tank up to strength. The nitric acid is controlled by determining the loss of weight from a standard-sized piece of the steel in use, during a definite time of immersion. The weight loss should be of the order of 4 to 6 gm. per sq. ft. If the desired weight loss is not obtained with 20 per cent nitric acid in the specified time an extension of time rather than increase in concentration of acid is recommended.

5. Cold-water rinse of the overflow type.

6. Sulphuric-acid pickle.—This is a second pickle of the same concentration and operating at the same temperature as the one previously used in 2 above. Immersion time is half a minute to a minute. The purpose of this step is the removal of ferric salts formed during the nitric-acid pickle.

7. Cold-water rinse.—This again is an overflow type.

8. Nickel deposition.—The solution in the nickel tank is made up as follows:—

|   |                     |
|---|---------------------|
| Nickel sulphate (single nickel salts) ... | ... 4 oz. per gal.  |
| Sodium acetate ...                        | ... 1½ oz. per gal. |
| Sodium hypophosphite ...                  | ... ½ oz. per gal.  |
| Operating temperature ...                 | ... 130° F.         |
| Time of immersion ...                     | ... 2 to 3 minutes  |

Nickel deposition should be in the range of 0.10 to 0.15 gm. per sq. ft. This is from two to three times the amount normally deposited in a galvanic nickel dip. In addition the nickel coating deposited by the chemical reduction method is more continuous than that produced by galvanic displacement. The deposition of nickel is determined primarily by the concentration of sodium hypophosphite and the temperature of the bath. The pH value of the solution as made up will be in the neighbourhood of 5.5. As the tank is used the pH will drop and must be adjusted by the addition of ammonium hydroxide. The optimum pH range is 3.5 to 5.5.

The sodium acetate acts as a buffer in the solution, and requires no control and need not be replenished.

9. Following the nickel tank a further water rinse is necessary after which the ware is dried.

In the plant previously mentioned which employs this process commercially, slight modifications have been made, and the full method is given below. The ware is formed in good quality

enamelling iron and then processed as follows:—

1. Alkali cleaner:—
  - (a) Boiling solution—full strength.
  - (b) Boiling solution—half strength.
2. Hot-water rinse.
3. Cold-water rinse.
4. Hot sulphuric-acid pickle. Acid concentration 6 to 8 per cent temperature 150 to 160° F., time of immersion 3 minutes.
5. Cold-water rinse.
6. Nitric-acid pickle.—Acid concentration 20 per cent operating at room temperature. Time of immersion  $\frac{1}{2}$  minute.
7. Cold-water rinse.
8. Cyanide neutralizer.—Sodium hydroxide 0.2 to 0.4 oz. per gal. Sodium cyanide 0.28 to 0.56 oz. per gal. Temperature 130 to 140° F. Immersion time 3 minutes.
9. Cold-water rinse.
10. Nickel deposition—as specified in Ferro-Republic process previously discussed. Immersion time 1 minute.
11. Boiling rinse made up of very dilute solution of sodium hydroxide.
12. Dry in a hot air tank.

It will be noted that the practice here departs from the original specification in so far as the second immersion in sulphuric acid is eliminated and is replaced by a cyanide neutralizer, while the final rinse instead of being just a cold-water rinse is a boiling dilute solution of sodium hydroxide.

The ware going through the pickling cycle is kept in batches, and a piece from each batch is coated, fired and tested for adherence before the batch is released for processing. Storing pickled ware for a reasonable length of time appears to have no detrimental effects on either finish or adherence.

The coating is applied by an automatic spraying unit. The backs of the articles, in this instance wall tiles, are given a light dust and a full coat of approximately 30 to 35 gm. per sq. ft. is sprayed on the face side. Firing is by a continuous furnace at a normal time/temperature cycle for the enamels in use.

The finish produced in one coat is not of a very high order, and it is doubtful if the average one-coat result would be accepted for domestic appliances. In two or more coats, however, the finish is excellent.

As in the case of the titanium-steel process the surface finish in two or more coats appears to be generally superior to that obtained over conventional groundcoat. Likewise resistance to impact and torsional damage is greatly increased.

At another plant producing sanitary ware, on which it was not possible to gather first-hand information, a further variation on the Ferro-Republic process is in use. Here after degreasing,

in this case larger articles of heavier gauge, the ware is shotblasted. A very fine grade of shot and an airless Wheelabrator type of machine are used. This blasting cycle produces the deep etch on the metal permitting the nitric-acid pickling to be dispensed with.

Following on the shotblast a normal hot sulphuric-acid pickle is used, as also is the Ferro-Republic nickel-dip procedure. It is claimed that this metal preparation produces a superior adherence and freedom from defects in the enamel surface.

No attempt to produce one-coat work is made. The first coat, or "white groundcoat" as it is termed, reclaimed titanium enamel, the second coat is the same enamel freshly milled but containing no reclaim.

The finish produced in two coats sets very high standards in appearance and durability. A further advantage claimed for this process is the fact that it simplifies the enamelling procedure by eliminating groundcoat and groundcoat operation.

Typical mill additions for this class of enamelling are given in the previous paper but reclaim used as a first coat is prepared as follows:

|                                  |     |
|----------------------------------|-----|
| Blunged and roto-sprayed reclaim | 100 |
| Potassium carbonate              | ... |
| Sodium nitrite                   | ... |
| Methyl violet dye                | ... |
| Urea                             | ... |

The reclaim is milled for a short time in a mill which is double charged so that the fineness is not affected.

The authors wish to express their appreciation and thanks to the directors of Ferro Enamels Ltd. for permission to prepare and present these papers, and for the facilities provided during their recent visit to the United States to study the progress of the direct-on-steel programme in that country.

## DISCUSSION

Dr. B. K. NIKLEWSKI (Main Enamel Manufacturing Co. Ltd.) said that in Columbus, Ohio, a paper was presented by Paul Cecil of Strong Mfg. Co. dealing with a process of one-coat application on non-premium steel in which it was claimed that for half a year they had applied titanium enamel direct to a normal enamelling iron and had produced components for the Westinghouse Company who demanded very high standards of finish. He had looked for further developments and for some details of the process, but had not found them, and he asked if Mr. Murdoch or Mr. Zick had any more information concerning this process.

A year ago Mr. Ernest Hommel, in his paper presented to the I.V.E., mentioned the Eckel Romine process, and he claimed that two fac-

ories were working with good results using this process.

With regard to the British development of the application of enamel directly to iron, Dr. Niklewski said he was fortunate to have been engaged in some research work in conjunction with the sheet rollers in this country in the development of Nitec steel, and his firm were using it for the self-mottling finish; they were the first in this country to use that finish for cookers, and others were also using it with considerable success. His firm had only a certain amount of the steel, but were using it in parallel with the nickel-dip process. Both metals, Nitec steel and ordinary metal with nickel dip, gave excellent results. At one period there was some difficulty in production owing to a too heavy nickel deposit on Nitec steel and consequent flaking-off of nickel, but that was found to be due to a flaw in production, and the steel manufacturers had overcome this difficulty.

It was interesting that in the course of the research with which he had been concerned they had tried using very deep etched metal covered with nickel and were getting some very promising results. They were still researching and further developments could be expected.

Those who were concerned with the application of enamel direct to steel did not appear to realize the fact that as the covercoat became thinner and thinner, a scratch or a small indentation could be seen more and more easily, so that any saving which would be effected by eliminating the groundcoat would be partly absorbed by the greater care necessary in shepherding the components through the production process. There was no immediate monetary gain to be expected, and there would have to be a great deal of perseverance and even some loss in production until something cheaper than the conventional finish could be developed.

Dr. Niklewski expressed the view that much more could be done not only by the frit manufacturers and the enamellers, but also by the steel manufacturers. Recently he had learned that Armco would put forward titanium steel at a very reasonable price within a year or two, and that would completely change the picture in regard to the application of one coat direct on to the metal. He had a feeling, from information he had received, that the difficulties could be much reduced, with the collaboration of the steelmakers.

Mr. ZICK, referring to the process of the Strong Manufacturing Co., which was reported on by Mr. Paul Cecil, said that unfortunately, shortly after Mr. Cecil's paper was presented, the company had ceased operations owing to trade union troubles and the process apparently had gone with the company.

He was well aware that the Eckel Romine process had been mentioned by Mr. Hommel to the Institute in 1953. But Mr. Murdoch and himself had found only two genuine cases of production by the direct-on process in the United States from the east coast to the west, even though they had spent a good deal of time seeking evidence of the application of the process in production.

Mr. H. LAITHWAITE, (Metal Porcelains Ltd.) discussing some of the work that had been done on the problem under consideration, said that his firm in common with many others, had done more than a little work and had found no great difficulty in producing excellent specimens in white direct-on, in the laboratory. To translate that result into production had so far proved impossible. They had no special steels and they had had to face the fact that production in certain circumstances had to be done on two or three different grades of steel at one and the same time, which was a complication.

Speaking of de-greasing operations, he said that some de-greasers were more effective than others and, having regard to the variety of steels that had to be used and, one imagined, of the materials on the surface, quite a bit of trouble had been experienced in ensuring that the surface was perfectly clean. That applied to normal production, but it applied ten-fold to direct application.

Agreeing that there was a need for an etched surface, he said that nitric acid was one way of providing it; there were other possibilities and he asked if the authors had considered using a chromate bath, which in his view had one advantage over nitric acid. His company had automatic plants, and although a very short immersion in nitric acid would do what was required, it did not fit in with their particular plants. A small addition of dichromate, about 1 per cent, to sulphuric acid, was used.

On the question of application, from his experience he would put the figures a little higher than had the authors for whites direct-on. Experiments suggested that 0.15 or 0.2 gm. per sq. ft. was about right, although for other purposes, where the nickel dip was used, his company's standard figure was about 0.1 gm. per sq. ft.

While he had not first-hand knowledge of the Ferro-Republic process, he had had some limited experience of Nitec steel and he made the point that the nickel-dip process cost roughly 12s. per ton of metal treated, which compared with £8 per ton for the Nitec steel. Using the nickel dip under the conditions applied at his works, better results were obtained than with Nitec steel.

Commenting on the stress which had been laid on the need for control, he said the solution must



be carefully controlled, and so on, and the enamelling industry as a whole had to face up to that problem. If they were to advance technically they must accept the implication that the producer could no longer rely on the methods he had used for many years—he must have adequate control. The nickel-dip process, by comparison with some of those suggested, was fairly simple, but it would demand a degree of control of pickling which the orthodox processes should not require.

He wondered whether, as an intermediate step, the industry might consider going further along orthodox lines. His company had given thought to that in the direction of applying an orthodox groundcoat, thinner and yet thinner. Having studied the matter recently they had found that there was an advantage in using nickel dips for orthodox enamels. If they used the nickel dip they could use a thinner groundcoat than normal. They had experimented with groundcoats to see just how thin they could be, and they had been able to process parts in a simpler manner than in the past. He put it to the meeting, therefore, that possibly an approach of that sort as an interim measure would give at least some of the advantages which had been claimed for the direct-on process.

MR. MURDOCH said he had mentioned that there were other acid solutions besides nitric acid which might be used; and although he had not specifically mentioned the chromic-acid bath, it was another possibility and no doubt others would be brought forward which would give the correct deep etching required.

With regard to the use of thinner and thinner groundcoats, he had a feeling that that was happening now in a small way and that it would continue on a larger scale. In America the authors had seen a very thin groundcoat applied and, while still wet, a covercoat was sprayed on. This one-fire finish was not particularly good, but it was possible to put on a second coat and to make an excellent job. In that case there was no nickel coating, but he imagined that the application of a nickel coating would enable a still thinner covering of enamel to be used.

That was the sort of thing that was happening, and he had tried to emphasize in his paper that such possibilities had been almost forced forward by the titanium enamel development, which had gone ahead rapidly.

Mr. E. W. B. DUNNING (North Thames Gas Board) said that the gas industry was particularly interested in the problem of the chipping of the enamel on gas-consuming appliances. He was not asking for the enamel to be cheaper; he was asking for it to be better. He was even prepared to give way on acid resistance or something else if the extent of chipping could be reduced, because

chipping was becoming a very serious matter for the gas industry. It meant replacing parts immediately an appliance had been fitted or even during the process of fitting it.

It was felt in the gas industry that the thickness of the enamel was a very important factor, and it had been stated in the papers presented to the meeting that the aim was to get the enamel coating thinner and thinner. Quite recently they had made some investigations which had shown that normally, when enamelling had chipped, the trouble lay with the thickness of the groundcoat. The chipping did not occur on flat surfaces, but on the bends and corners; the swelling of the groundcoat was a very likely source of thickened edges, and a very much thinner groundcoat than normal would be very helpful from their point of view. They were not so much troubled about how many re-sprays were carried out; it was the ultimate total thickness of the enamel that concerned them.

Inspectors of enamelled ware were not able to measure the thickness of the enamel really effectively and checks that had been made when enamelled ware was received had shown that a lot of it became chipped at places where the enamel was thicker than it should be.

MR. MURDOCH commented that it was refreshing to hear a user say that he was not so much interested in the cost, but in the quality, of enamelled ware. He felt there could be no doubt that the use of a very thin groundcoat was coming forward, possibly without the use of a nickel dip or any form of nickel coating. He still felt, that the safest policy would be to use a very thin groundcoat and then cover it with one fairly heavy or even two lighter covercoat applications, particularly of a white titanium enamel.

Mr. A. G. JONES (Simplex Electric Co. Ltd.), confessed that he was horrified to hear references to the application of three and four coats of enamel, if present methods were used. It seemed to him that the enamelling process should require a maximum of two coats. The samples exhibited had no flat surfaces like those of cooker sides or splash plates, but had broken small areas which did not, of course, show up the defects so readily as would cooker sides. However, he asked the suppliers to continue by all means with their research to find a really good and economic one-coat enamel, which was what the industry was seeking.

In the paper he had noted that in connexion with titanium-bearing steel it was stated that the time interval between pickling and spraying should be kept down to a minimum, whereas in connexion with the Ferro-Republic process it was stated that to keep the material for a reasonable length of time appeared to have no detrimental



effect. The two statements were rather conflicting; his organization had found it best to have the ware sprayed as quickly as possible after preparation.

One of the advantages claimed for the Ferro-Republic process was that it simplified the enamelling procedure by eliminating the groundcoat operation. But had it eliminated anything? He understood that the groundcoat was cheaper. Admittedly the process eliminated any need to change the firing temperature, for he had gathered that the two or three coats were fired at one temperature.

While he had the feeling that enamelled ware produced by such a process did not suffer from chipping and other damage, he pointed out that no figures had been quoted. He asked, therefore, if it were possible for figures to be given from works and field reports comparing the supposedly one-coat enamelled ware with that produced by the normal process in respect of damage.

Mr. ZICK, discussing the comment concerning the application of two, three and four coats, said it would be appreciated that the papers presented were in the nature of a report of what was actually being done on technical and processing developments; he had tried to be a good reporter and to present the truth, in spite of the circumstance that it might not make the position look quite so rosy as it could be. It was a fact that work was re-coated as many as four times with that particular titanium-enamel process. It was also claimed by the company carrying out the process that 60 per cent of the work had one coat.

With regard to the point that splash plates and cooker sides were not exhibited, he said that unfortunately there were none of those components available which had been produced by the titanium steel process; those particular components for one of the appliances being manufactured were made with the conventional enamelling iron, not because the company could not produce them in titanium steel, but because they could not get enough titanium steel for the job. At the moment they were using titanium steel for jobs which normally suffered the greatest amount of chipping and other damage during storage and transit. When they had sufficient titanium steel they would use it also for other things.

With regard to the point that in the case of the titanium steel it was mentioned that spraying should be done as soon as possible after pickling, he said this was in fact done in the particular shop mentioned. It was found to be advantageous to keep the time interval between the metal preparation and coating to the minimum, chiefly because the products were susceptible to contamination from shop dirt in handling, and even rubbing in the stacks. For some components they

had gone so far as to design special racks on which to transfer the products from the pickle to the spraying operation.

With regard to delay between the metal preparation and the coating process in the Ferro-Republic process, he said it was brought about because it was the normal shop practice that no batch was released for processing until specimens from it had been tested. That involved a delay of approximately two hours as a minimum, but it appeared to have no detrimental effect whatsoever. From the purely theoretical point of view and from that of keeping free from trouble it might be advantageous to process immediately after metal preparation. A sample of a tub, finished in one coat by the Ferro-Republic process was available to show the type of finish produced.

As to the elimination of the groundcoat step, which was claimed to be an advantage, he said that in the case of a white coating one might consider it a doubtful advantage, but in terms of cost it might be a direct advantage. The elimination of one type of enamel in order to concentrate on another would lead to a simpler plant and a simpler plant layout, which should represent a saving in costs.

Unfortunately he had no figures comparing the extent of damage by chipping in products of the Ferro-Republic process with that in products of the normal process. In the case of enamel on titanium steel it was claimed that there was an appreciable advantage in that respect, that the material did not suffer nearly so much chipping as did that produced by the normal process, and the producers were able to simplify the packing cases because the enamel coatings were far more resistant.

Mr. J. H. GRAY (Stewart and Gray Ltd.), confessed that as a result of the various comments he had not got a clear picture of the position. Mr. Murdoch had stated in his paper that the Ferro-Republic direct-application process was a metal treatment process which permitted the application of a wide variety of finish coats direct to steel. Later, it was stated that there was still quite a lot of work to be carried out in this connexion, and this of course he could appreciate. He did, however, ask the authors to state as a result of their investigations, what troubles were being experienced with direct application. He felt that it was a long way from being a straightforward proposition, otherwise the process would be more widely adopted. Was the main trouble flaking off of the enamel after fusing, boiling up of the enamel, or some other equally serious problem?

Regarding the figures comparing the costs of applying ground coat and cover coat to standard steel, against the costs of applying a finish coat

direct to titanium steel, he asked if it was quite true that the pressing and metal finishing costs were equal in both cases. He asked this question, as he felt it had been agreed earlier that far more attention had to be paid to the metal finishing when titanium steel was in use.

MR. ZICK replied that there were certain defects, certain disadvantages, which were holding up the wholesale adoption of the Ferro-Republic process. One of the things the authors had discovered in their limited trials was the undesirable effect produced by the nitric-acid etch. He had mentioned that one of the alternative methods used was to replace the nitric-acid bath by the sand-blast. There was a certain degree of difficulty with fish-scaling on some types of ware, which he supposed might be attributed to over-pickling, and there was also some difficulty with pin-holing as the result of the residue left on the steel after the nitric-acid etch.

The comparative cost figures were not his; they were actually published figures.

MR. T. TIDDER (Stewart and Gray Ltd.), speaking on the method of application of the first coat in the two-coat process, enquired if this first coat was a white ground coat and if so, was it applied by dipping or spraying. If spraying was the normal method of application, he considered it would be much more expensive than dipping. He also asked for information concerning the fineness to which this first coat was ground and also the fused thickness.

MR. ZICK replied that the first coat was applied by spray. The products in that particular case were sanitary ware and they were of such sizes and shapes that it would be impracticable to dip them.

The mill additions were similar to those used for the conventional type enamelling of covercoat. The thickness of the first coat was in the region of 0.003 in.; the figure of 0.005 in. which had been mentioned applied to one-coat enamelling on titanium steel.

MR. W. H. F. TICKLE (Manchester College of Technology) said he had gathered that titanium-stabilized steel cost £14 per ton more than ordinary enamelling steel in the U.S., whereas Nitec cost £8 per ton more than ordinary enamelling steel in this country.

He was also interested in the cost of putting on the nickel coating by the reduction process. If £8 per ton surcharge was unacceptable he wondered if there was anything in it from the financial point of view to justify the steel people really trying.

MR. ZICK said there seemed to be some confusion as between the titanium steel and the Ferro-Republic processes. They were two completely separate and individual processes.

The figures in his table referred to the titanium-steel process, which did not employ the reduction method of nickel flashing; the nickel was applied by the normal dipping method.

In Table I, the costs of the nickel flash and the pickle were combined and one could not split them; the figure in the two cases that were compared was 0.0643 dollar (6.43 cents.).

TABLE I

Comparative cost figures (in dollars) of applying groundcoat and covercoat as against finish coat direct to titanium steel.

|                       | Ground-coat plus Covercoat | White on Titanium Steel |
|-----------------------|----------------------------|-------------------------|
| Metal blank           | 0.2248                     | 0.2766                  |
| Draw and metal finish | 0.0880                     | 0.0880                  |
| Pickle                | 0.0643                     | 0.0643                  |
| Ground coat           | 0.2253                     | 0.0000                  |
| Cover coat and labour | 0.4612                     | 0.4808                  |
|                       | <hr/> \$1.0636             | <hr/> \$0.9097          |

Saving \$0.1539.

MR. TICKLE pointed out that the £14 per ton extra cost of the titanium-stabilized steel in no way reduced the cost of the enamelling process, except where the grip coat was eliminated when some compensation was offered.

He gathered that in the process using titanium-stabilized steel, a nickel flash was applied. When using the orthodox method we still might apply a nickel flash but we had not paid the extra £14 per ton for the steel.

The Nitec steel in this country was already nickel treated, and that cost only £8 per ton more than ordinary enamelling steel. He asked how much the prices of the steel had to be reduced relative to the prices ruling in the U.S. in order to make the enamelling operation economic in the United Kingdom.

MR. MURDOCH pointed out that there were additional steps to be taken in the process where one used regular enamelling steel and put on a nickel coating by the reduction method. There was the cost of the additional tank used, whether a nitric-acid bath or any other; that was an additional cost over and above the regular pickling procedure, but he could not say what that cost would be.

He understood that there was really no difference in the cost of applying the nickel coating whether one used the reduction process or the ordinary nickel flash, but the cost of the additional acid tank had to be taken into account.

DR. NIKLEWSKI said that first must be borne in mind the claim that titanium-containing steel

would not blister. It would not give more adhesion than the ordinary enamelling steel; but because it would not blister and would not evolve gases, a very thin coat of enamel could be applied to it. Those operating the Ferro-Republic process were using the regular enamelling steel and accepted the handicap of the evolution of gas, and that was why they could not claim 100 per cent success; they could not overcome the blistering. Even a mottle enamel could not cope with the heavy gassing of the steel.

Discussion of costs was rather futile at the moment because the costs of the processes were mixed up with the price of steel. When there was more of the special steel available its cost and its price would be reduced; within a year or two it would be available much more cheaply than at present.

Mr. S. E. A. RYDER (Stoves Ltd.) commented that two separate problems had been presented, namely the production of a satisfactory white finish in one coat direct on titanium steel, and the application of white enamel direct to ordinary enamelling steel.

In the case of the first process by using titanium-killed steel a satisfactory finish could be obtained with a thickness of enamel of only 0.005 or 0.006 in. and everyone must agree that this would be most desirable even if it cost more to produce than the present finish white enamel because of its greater durability. The replacement of parts of appliances due to damage of enamel in transit or after only a short period of use was a very costly problem to appliance makers, and if one-coat enamel on titanium steel reduced the necessity for such replacements an appreciable increase in the cost of the enamelling process would be justified. Unfortunately however, such steel was not available in this country at present so while the process was extremely interesting, their interest could only be academic.

Turning to the application of white enamel direct on to ordinary enamelling steel, he said he could not see what advantage would be gained by carrying out the Ferro-Republic process as outlined by Mr. Zick. He understood from the lecturer that one coat of enamel on the steel did not provide a satisfactory finish for high grade articles, and two coats were necessary. Presumably the thickness was then of the same order as that of a coat of white over conventional groundcoat and no doubt resistance to chipping was also of the same order.

A possible snag which had been mentioned in connexion with the Ferro-Republic process was the need for a nitric-acid bath. The chemical engineering problems involved in such a plant were quite considerable. It had been stated that something like 6 gm. per sq. ft. of iron had to be

dissolved and this represented approximately 1 per cent of the sheet metal immersed in the acid. The amount of nitric acid which would be used would be very considerable, and difficulties in supply would almost certainly arise, while the problem of disposing of such large volumes of spent nitric acid would be very great indeed.

On Mr. Zick's point that sandblasting had been applied to produce the necessary surface roughness, Mr. Ryder commented that his company had tried stripping vitreous enamel from sheet-metal surfaces by shotblasting and the results were very poor. In this country, of course, sandblasting would not be tolerated and he asked therefore whether the process referred to by Mr. Zick was actually sandblast or whether some other abrasive was used.

Mr. ZICK said he understood that the material was literally sandblasted. Unfortunately, first-hand information was not available, but he understood that trials had been made with a very fine grade of shot, and that lately the work was actually done with sand.

Coming to the question as to why one coat of white direct on to steel by the Ferro-Republic process was unsatisfactory, he exhibited a one-coated tile and some plates and said that in some cases the gloss was not so high as in others, and in certain cases also there was a certain amount of pin-holing.

As to the need for the application of two coats, he said the products were sanitary ware and the standard of finish had to be very high indeed, and it must be acid-resisting. It was as much a matter of choice as of necessity that two coats were used.

He could not give advice, he concluded, on how to dispose of spent nitric acid.

Mr. D. JACKSON (Stavely Iron and Chemical Co. Ltd.), referring to methods of deep etching, said it seemed that something like a gallon of nitric-acid solution would have to be discarded after 40 sq. ft. of metal had been treated, and to make up a gallon of 20 per cent nitric-acid solution after only that amount of treatment would seem to be very expensive. He could quite understand why that was one of the factors which was not helping in the development of the process. Basically it seemed that they were trying to do the same thing as in the titanium-steel process without incurring the extra cost of the titanium steel.

The vitreous-enamelling industry had discovered that batch treatment in the oven was not best for enamelled ware, and each component was passed through on a chain. Yet for some reason they had not been able to extend their thinking in the same direction as the plating industry by putting a single component through the pickling plant. That would overcome a lot

(continued in page 42)



### Direct Application of Finish-Coat Vitreous Enamels to Sheet Steel

(continued from page 41)

of difficulties which arose from packing the ware in baskets and would present the possibility of deep etching anodically at 50-100 amps per sq. ft. in a cold 50 per cent solution of sulphuric acid. He asked what the authors thought of the merits of a deep etch produced in such a way.

MR. MURDOCH replied that in reviewing his paper he had mentioned at least two other pickling solutions which could be used for deep etching, and Mr. Laithwaite had talked about chromic acid.

The use of nitric acid was just one of the means of deep etching, and possibly some of the other methods would be cheaper. He did not know the relative costs of sand blasting against nitric acid; but those were processes which were actually being used. He was perfectly certain that the people in the places where they had seen those things happening would effect modifications and improvements in the course of time, because they were really going into those problems. Expense must be a consideration and he was sure that people who were producing hundreds of thousands of articles according to the processes given would not go on losing money.

MR. ZICK, referring to some of the enamelled tiles he had exhibited, said their dimensions were  $4\frac{1}{2}$  in.  $\times$   $4\frac{1}{2}$  in. and 25,000 were processed each day for an expenditure of 26 gallons of nitric acid.

### SODIUM-HYDRIDE DESCALING

#### Contract Plant in Operation

Durtnall and Hipwell Ltd., Staines, Middx., who provide a comprehensive range of metal pre-treatment services, including processes for the purpose of descaling, derusting, degreasing and depainting both ferrous and non-ferrous materials, and a service for the metal blacking of steel components, have recently installed a sodium-hydride plant. This installation comprises a number of processing tanks capable of handling work which may be contained in vats 6 ft. long  $\times$  4 ft. wide  $\times$  4 ft. deep. The sodium-hydride process is licensed by the company from Imperial Chemical Industries Ltd., and this particular plant is the first of its type in Great Britain to be operated solely as a contracting service for the engineering industry and allied trades.

The process can be used for descaling and derusting, for example, titanium sections after heat treatment, crankshafts, etc., stainless steel, Nimonic pressings, forgings, copper wire and tube, etc., and is also very suitable for the desanding of ferrous and non-ferrous castings.

### Institute of Metal Finishing A.G.M.

(continued from page 15)

#### Honorary Treasurer :

F. L. JAMES.

#### Honorary Secretary :

S. WERNICK, Ph.D., M.Sc., F.R.I.C., F.I.M.

#### Members of Council :

In accordance with the Articles of Association of the Institute (Articles 42/43), the following Members of Council continue in office for the forthcoming Session :—

W. F. B. BAKER, A.M.I.E.E.

H. CANN.

L. B. HUNT, Ph.D., M.Sc., A.R.C.S., F.R.I.C.

L. MABLE.

J. M. SPRAGUE, M.Sc., F.R.I.C.

A. W. WALLBANK, B.Sc., F.R.I.C.

As a result of the Ballot held recently, the following have been elected to fill the three vacancies on the Council, thus bringing the total number of ordinary Members to nine in accordance with Article 33 of the Articles of Association :  
D. N. LAYTON, Ph.D., M.Sc., A.R.C.S., D.I.C., A.Inst.P.

R. T. F. McMANUS  
F. WILD, A.I.M.

#### Ex-Officio :

E. E. LONGHURST, Ph.D., Chairman, London Branch.

R. G. HUGHES, Chairman, Midland Branch.  
W. A. Bowker, Chairman, Sheffield and North-East Branch.

B. J. JONES, Chairman, North-West Branch.

S. A. J. MURRAY, Chairman, Scottish Branch.

A. A. B. Harvey, M.Sc., A.R.I.C., Chairman, Organic Finishing Group.

### The Institution of Chemical Engineers' Examinations

THE Institution of Chemical Engineers has recently published new "Regulations for the EPI Admission of Student, Graduate, and Corporate Members, and for the Examination of the Institution." These regulations contain the syllabuses for the examination which is to be held for the first time in 1956. The preliminary or Part I of the new examination will, however, also be held in 1955, immediately before the last examination in Papers C, D, E, and F, of the present examination as described in the Institution's pamphlet "Hints to Candidates." The closing date for entry to both the present and new examination is June 1 in each year.

Further particulars may be obtained from the General Secretary, The Institution of Chemical Engineers, 56, Victoria Street, London, S.W.1.



# NEWS REVIEW

## EPIKOTE RESINS AND THEIR USES

EXHIBITION ORGANIZED BY SHELL CHEMICALS LTD.

AN exhibition to demonstrate to industry the wide variety of practical uses to which "Epikote" resins are being put, either incorporated in surface-coating formulations or in the fields of plastics and adhesives, was organized recently in London by Shell Chemicals Ltd. The exhibition was subsequently staged at the Engineering Centre, Birmingham on January 11, 12 and 13, and can also be seen at the Central Hall, Glasgow on January 25 and 26, and in the Bleachers Association Assembly Hall, Blackfriars House, Parsonage, Manchester on February 2 and 3. Invitations to these exhibitions, which are of interest to all concerned with surface coatings and plastics, can be obtained from the divisional officers of Shell Chemicals Ltd., at 28, St. Enoch Square, Glasgow, C.1., and 42, Deansgate, Manchester 3.

"Epikote" resins are produced synthetically from two chemicals, epichlorhydrin and diphenylolpropane, and are of the type known to industrial chemists as epoxide or epoxy resins.

Their manufacture by Shell is an outcome of the Shell Group's leading position in the production of chemicals from petroleum, a field in which it has been the chief pioneer. One of the outstanding achievements of Shell chemists has been the successful manufacture of synthetic glycerine and epichlorhydrin is an intermediate product of the process involved.

Production of these resins began in the United States in 1949, and is now running at about 11,000 tons per annum. A sterling area plant came into production at Pernis in Holland eighteen months ago and another now nearing completion, in the Shell chemical plant at Stanlow, Cheshire, will be producing by mid-1955.

At present the main outlet for these resins is in surface coatings including paints, lacquers, stove enamels, varnishes and printing inks, but, as the exhibition demonstrates, they have great practical application as casting and laminating resins.

For use in surface coatings "Epikote" resins are of great importance because they combine the desirable qualities of adhesion, flexibility, toughness and resistance to chemicals to a degree which it was impracticable, hitherto, to achieve in one finish (see illustration on right). Earlier synthetic resins made it possible to formulate coatings with some of these qualities; "Epikote"-based formulations can

have them all at the same time. In general, "Epikote"-based coatings impart harder wearing finishes than have been practicable in the past. Although derived from petroleum the characteristics of the raw material are completely changed in the processes involved. Thus neither the resins or the coatings made from them are inflammable in the manner of petroleum. In heat-resisting properties "Epikote" finishes are again superior to most of the conventional coatings.

"Epikote" resins will probably always tend to be dearer than the alkyds and other resins currently in use because the cost of the raw materials is high. But although, in many cases, the cost of a gallon of an "Epikote" finish is higher than another the extra expenditure will often be balanced by economies in application due to superior qualities.

For example, two or three coats of an "Epikote"-based product will in many cases give a finish better than one involving as many as six coats of other types. In other cases, and particularly where conditions of wear and tear and atmosphere are specially arduous, the less frequent need for repainting or the fact that no other type of coating would give the necessary protection even for short periods, more than justifies the initial cost. Furthermore the use of an "Epikote"-based finish may sometimes make it possible to replace an expensive material such as stainless steel with a less costly alternative.

It is worth noting that the superior adhesion characteristics of "Epikote"

coatings makes them particularly attractive for use on such 'difficult' materials as aluminium, magnesium and light alloys.

The two principal uses for "Epikote" resins in the plastics field are as casting and laminating material. The casting applications are of particular interest to the electrical industry for "potting" techniques.

The range of application of these resins was amply demonstrated at the exhibition. The applications include, primers and finishes for refrigerators, washing machines, kitchen equipment etc., where their resistance to chemicals give protection against damage by fruit juices, alcohol, disinfectants, etc., etc., and in particular modern detergents. Other uses on show are the coating and "potting" of electrical equipment, internal and external coatings for collapsible tubes, anti-corrosive paints, coatings for the protection of chemical plant, yachts, concrete and wood floors.

*The remarkable adhesion and flexibility of Epikote-based surface coatings can be seen in the photograph below. The aluminium tooth-paste tube on the left has been completely "telescoped", and then (on the right) pulled out again. No cracking of the surface coating took place.*





## MEASUREMENT OF ATMOSPHERIC POLLUTION

### London Station Set Up

**A**N observing station for measuring the smoke and sulphur-dioxide pollution in the London atmosphere has been established in the Science Museum by co-operation with the Fuel Research Station of the Department of Scientific and Industrial Research. The station is one of a number that are being established to permit a more detailed examination of atmospheric pollution in London and elsewhere.

The sampling equipment is displayed as a working exhibit in the Meteorology gallery. The smoke particles are captured on filter paper through which air is drawn from just above museum roof level, by means of a small electric pump. As a result, a grey stain appears on the filter paper, the intensity of which is a measure of the degree of smoke pollution. The same air is bubbled through a weak solution of hydrogen peroxide where the atmospheric sulphur dioxide is dissolved to form an acid solution, the strength of which is measured by standard chemical methods.

Observations of smoke and sulphur-dioxide pollution are made daily by a member of the museum's staff and reported to the Fuel Research Station who are in charge of the investigation.

## LECTURE COURSE ON VITREOUS ENAMELLING

**T**HE North Staffordshire Technical College, Stoke-on-Trent, began on January 4, a series of twelve lectures on the production of vitreous-enamelled ware. The lectures which are being held on Tuesdays from 5.15 to 6.30 p.m. will end on March 22. The general subject titles for the lectures are as follows: enamelling-plant construction and layout, supply of metal components, practical aspects of design of components with regard to enamelling and assembly, preparation of metal, frit manufacture, milling, control of operations, application of enamel, drying equipment, burning, de-enamelling, organization of inspection. Each lecture deals fully, where required, with factory and personnel problems, all types of equipment, costing, etc.

## Society of British Paint Manufacturers Tenth Annual General Meeting

**A**T the Tenth Annual General Meeting of the Society held at the Dorchester Hotel, London, on Tuesday, November 9, 1954, it was announced that Colonel F. W. Jones and Mr. C. D. O'Sullivan had been re-appointed president and vice-president respectively, for the year 1954/55.

The five vacancies on the council were filled by the election of the following:—

Mr. T. S. Dally (Pinchin, Johnson and Associates Ltd.)

Mr. J. P. Halpin (Lewis Berger (Gt. Britain) Ltd.)

Mr. C. A. F. Hastilow (Docker Bros. Ltd.)

Mr. H. Leigh (W. and J. Leigh Ltd.)

Mr. C. R. Petrie (International Paints Ltd.)

Mr. F. A. Bignell was appointed honorary treasurer, and Messrs. Lithgow, Nelson and Company were appointed Auditors.

During his presidential address, Col. F. W. Jones, said that there was little doubt that in the paint industry during the previous twelve months the new scheme for the supply of building paints to Government Departments had been of prime importance. He criticized the fact however, that the paint industry had not been invited to submit their comments until the Government had devised a complete plan. The Society had asked for the scheme to be postponed for twelve months but were successful in getting the postponement only until March 1.

The president also referred to the fact that the Building Paint Advisory Council was one year old on October 14, 1954 and it was with pleasure that he was able to report that the Council had accomplished its first year's work with astonishing success. He paid tribute to Mr. Ashley Hall, the first chairman of the Council, and to Mr. C. D. O'Sullivan, who took over the office of chairman when Mr. Hall assumed presidency of the National Paint Federation.

Col. Jones pointed out that the Council is an industry organization

and is one of a number of bodies in which the members of the National Paint Federation and the Society of British Paint Manufacturers discuss topics in a spirit of industrial well being and without a thought of the organization to which members each individually belong.

After welcoming new members of the Society, the president paid tribute to the Society's secretary, Mrs. Miriam Bruce, and pointed out that the Council had ensured her continued valuable service.

The president continued by referring to the paint industry Colour Ranges Committee and the widely accepted colour range of 101 colours, and to the formation of the Decorative Paints Group of the Society. This new Group had already met on a number of occasions under the chairmanship of Mr. C. D. O'Sullivan.

The president concluded by making reference to the visit to Canada of the Society's general manager, and by thanking honorary officers and other members of the Society's staff for the excellent work they had carried out during the year.

## "CORROSION IN THE HOME"

### Exhibition to be held at Battersea Polytechnic

**A** PUBLIC exhibition demonstrating materials and methods used in limiting corrosion in the home will be held in the Great Hall of Battersea Polytechnic, Battersea Park Road, London, S.W.11, on January 21, 1955, from 10 a.m. to 4 p.m. Admission is free, and no ticket will be necessary. There will be a private showing on the previous day to members of the Corrosion Group of the Society of Chemical Industry, who are organizing the exhibition.

Metals have innumerable household uses. To mention only a few examples: outside the house metal may be found in windows, rainwater gutters and pipes, gates and fences; inside, there

may be water cisterns, pipes, cooking vessels, cutlery, kitchen tools, stoves, washing machines, buckets and shovels. The uses are diverse but they have one feature in common; if the metal or the protection given to it is not well chosen, its appearance and usefulness will deteriorate through the action of corrosion.

The articles and utensils included in the display will fall into four categories: building materials, plumbing, domestic equipment and tools, and ornamental metalware, providing a comprehensive demonstration of the formidable extent of the corrosion problem and the protective methods being developed to combat it.

# THE PROTECTION OF STRUCTURES

Symposium organized by the Corrosion Group  
of the Society of Chemical Industry

A SYMPOSIUM on "The Protection of Structural Steel", organized by the Corrosion Group of the Society of Chemical Industry, will be held in the lecture-theatre of the Institution of Civil Engineers during the days of Thursday, March 31 and Friday, April 1, 1955. The papers to be presented will include accounts of practical experience and of research with protective coatings gathered from several countries.

Some details of the proposed papers are shown in the list which follows, covering contributions from France, Belgium, Holland, Sweden, and the U.S.A. as well as Great Britain.

## Practical Experience

W. E. Ballard (Metallisation Ltd.)—  
and F. A. Rivett (Schori Metallising  
Co.)—*Practical Experience of Protection by Sprayed Metal Coatings.*

J. Bigos (Steel Structures Painting Council, U.S.A.)—*Current Good Paint Practice for Steel Structures in U.S.A.*  
F. Fancutt (British Railways)—  
*Painting and Protection of Steel Structures (Great Britain).*

F. R. Himsforth (Imperial Chemical Industries Ltd., Billingham Div.)—  
*Protection Problems in Chemical Plant.*  
L. A. Ravald (North Thames Gas Board)—  
*The Preservation of Steel on Gas Works in Great Britain.*

W. A. Johnson (United Steel Co's., Ltd.)—  
*Some Factors in the Protection of Steel in and at the Steelworks.*

## Comparative Tests

C. Decheaux (Société des Peintures, Paris)—  
*Principles of Protective Painting.*

K. F. Trägårdh and P. Nylén (Swedish Corrosion Commission)—

*Exposure Tests of Paints and Zinc Coatings in Sweden.*

J. C. Hudson and J. F. Stanners (British Iron and Steel Research Association)—  
*The Formulation of Priming Paints for Structural Steel.*

H. W. Talen (Verf-Instituut, Delft, Holland)—  
*Physical Examination of Paints in Relation to their Practical Performance.*

M. Van Rysselberge and D. Bermann (A.B.E.M.)—  
*Results of the Researches Carried out by the Belgian Corrosion Commission.*

Of these authors, all except Dr. Bigos are expected to be present, and an additional distinguished visitor from overseas will be Mr. F. L. LaQue.

Further details of the arrangements for the meeting will be published later, but non-members of the Corrosion Group who wish to receive a copy of full notice of meeting and registration form, when it becomes available, are invited to apply to the hon. secretary of the Group, Mr. S. C. Britton, The Tin Research Institute, Fraser Road, Perivale, Greenford, Middlesex.

# U.S. MARINES AID HUNT FOR MISSING CORROSION SPECIMENS

Test Racks Damaged by Hurricane

EQUIPPED with mine detectors, United States Marines from Camp Lejeune, N.C., are literally seeking buried treasure at the site of the International Nickel Company's sea spray corrosion test racks on the Atlantic Coast at Kure Beach, North Carolina. The Marines are assisting in the search for thousands of valuable specimens torn by a recent hurricane from racks 80 ft. from the ocean and buried deep in the sand by wind and waves that reduced the area to a shambles.

The racks formed part of Inco's "Kure Beach" Corrosion Testing Station, established in 1935 and recognized today as the most extensive research project of its kind in the world. The station embraces facilities for studies on the behaviour of materials in sea air at Kure Beach and salt water

at nearby Harbor Island. Activities at this station have yielded information on how bare and coated metals, woods, plastics and cordage are able to resist the corrosive effects of salt water, salt spray and sea air. They have resulted in a saving to industry of many millions of pounds.

The destructive effects of the waves at Kure Beach were augmented by the battering action of floating piling and timbers from fishing piers smashed by the storm. The rack supports with their concrete anchors were wrenched out of the ground. The pipe frames were bent and twisted completely out of shape by the fury of the wind and the force of the waves. Waves piled sand up to a depth of about three feet over that portion of the test site area that was not washed away.



## RECENT DEVELOPMENTS IN METAL FURNISHING Course of Lectures

ON January 3, 1955, a series of lectures under the title of "Recent Developments in Metal Finishing", commenced at the Northampton Polytechnic, London, E.C.1. The first lecture, given by E. A. Ollard, A.R.C.S., F.R.I.C., F.I.M. (B.N.F. M.R.A.) dealt with "Recent Developments in the Electrodeposition of Nickel and Chromium", and the subsequent one, on January 10, was entitled "The Electroplating of Precious Metals", the lecturer being S. W. Baier, A.R.I.C.

The remainder of the lecture series is as follows: January 24, "The Electrodeposition of Tin and Tin Alloys", by R. M. Angles (Tin Research Institute). January 31, "Metal Spraying and Its Application", by W. E. Ballard, F.R.I.C., F.I.M. (Metallisation Ltd.). February 7, "Zinc Coatings on Steel", by R. W. Bailey, M.A., B.Sc., F.I.M. (Zinc Development Association). February 14 and 28, "Lacquer and Synthetic Enamel Coatings and Stoving Finishes", by A. A. B. Harvey, M.Sc., A.R.I.C., M.Inst.W. (Briggs Motor Bodies Ltd.).

## PAINT FIRM OPENS NEW TECHNICAL CENTRE

MANDER BROTHERS LTD., 10 St. John's Street, Wolverhampton, paint and varnish manufacturers, are opening on January 19, a Technical Information Centre, which is to take the form of an interesting and factual display of technical information on paint problems. The company stress the fact that the Centre is not just another exhibition of paint finishes, and hope that it will satisfy the need for a centre where technical information relating to all aspects of paint usage can be obtained.

## Technical Sales Appointment

MR. L. F. PARSONS has been appointed technical sales representative for the London area, by Jenolite Ltd., 13-17, Rathbone Street, London, W.1.





## Meetings of the Month

January 17

**Institute of Metal Finishing.** "Anodic Oxidation of Copper," by S. G. Clarke, D.Sc., Ph.D., A.R.I.C., and "Sulphuric-acid Anodizing to Specification D.T.D. 910C" by J. F. Henley B.Sc., F.R.I.C., F.I.M., at the Northampton Polytechnic, St. John Street, London, E.C.1. 6.15 p.m.

January 18

**Institute of Metal Finishing (Organic Finishing Group)** "Open Forum"—Discussion, at the British Institute of Management, 8, Hill Street, London, W.1. 6.30 p.m.

**Society of Chemical Industry (Corrosion Group).** "The Inhibition of the Attack on Metals by Acids," by T. P. Hoar, M.A., Ph.D., at the Birmingham and Midland Institute, Paradise Street, Birmingham. 6.30 p.m.

January 20

**Society of Chemical Industry (Corrosion Group).** "Coversazione and Exhibition on the theme "Corrosion Prevention in the Home," at the Battersea Polytechnic, Battersea Park Road, London, S.W.11. 6.30 p.m.

**Institution of Production Engineers (Cornwall Section),** "The Protection of Metal Components Against Atmospheric Corrosion," by A. W. Marshall, F.B.H.I., at the Cornwall Technical College, Trevenson, Pool, Redruth. 7.15 p.m.

**Institution of Production Engineers (Southern Section),** "Modern Finishing Processes," by K. W. Abineri, B.Sc. (Hons.), at the Polygon Hotel, Southampton. 7.15 p.m.

**Institute of Metal Finishing (Midlands Branch),** Annual Dinner and Dance, at the Grand Hotel, Colmore Row, Birmingham, 3.

January 26

**Manchester Metallurgical Society** "Cathodic Protection" by W. F. Higgins, Ph.D., M.Sc., A.R.I.C., at the Central Library, Manchester. 6.30 p.m.

January 27

**Institute of Vitreous Enamellers (Midland Section).** Paper by J.L.S. Golding, at the Birmingham Exchange and Engineering Centre, Stephenson Place, Birmingham, 2.

January 28

**Institute of Metal Finishing (Sheffield and N.E. Branch).** "Bright Nickel," by A. F. Brockington, and "Barrel

## TRADE and TECHNICAL PUBLICATIONS

**"Titanium Oxide in Vitreous Enamels":** The demand for high-quality domestic and industrial vitreous-enamel finishes which combine pleasing appearance with superior practical properties, has led to the widespread use of titanium oxide in vitreous-enamel frits. The correct use of the non-toxic oxide produces enamels which combine, in one thin coat, complete opacity, high brightness, acid resistance and good mechanical and thermal shock resistance.

To assist frit makers in using titanium oxide to the best advantage, British Titan Products Ltd., Yorks, have published a comprehensive booklet which deals with the use of the oxide. Almost a textbook on the subject, this booklet, which consists of 64 pages of valuable information including, for example, frit formulations, testing methods, etc., etc., should be extremely useful to all users of frits.

**"Rust and Shipping":** This is the title of a 16-page illustrated brochure published by Jenolite Ltd., 43, Piazza Chambers, London, W.C.2. It describes the use of the company's products for the protection of the hulls, superstructure, and holds of ships of all types. Photographs show the results of trials on some vessels, parts of which were not treated, to give comparisons of results, after various lengths of time in service.

**Centrifugal Pumps:** Wilkinson Rubber Linatex Ltd., Camberley, Surrey, have issued an illustrated brochure, dealing with the "Linatex" pump which is used for the handling of abrasive solids in suspension, chemicals and effluents, etc. The design of this pump prevents metallic

contamination of the liquids inside the pump. Typical uses, construction, and typical installations are described and illustrated in the brochure.

**Filtration:** British Filters Ltd., Maidenhead, in association with the manufacturers Pritchett and Gold and E.P.S. Co. Ltd., draw attention in a new booklet to "Porvic" a new type of filter medium. This material is a pure unplasticized polyvinylchloride which is rendered porous by a patented process. It is claimed that the filter material guarantees 100 per cent retention of all solid particles above a pre-determined size, and the filtration rate is high.

**Acid-resisting Cement:** From J. H. Sankey and Son Ltd., Ilford, Essex, a leaflet has been received which describes the company's super acid-resisting cement, which is suitable for such uses as bonding brickwork in acid-laden soil, jointing sewage pipes and acid carrying pipes, jointing chimneys that carry acid fumes and for the construction of acid and leaching tanks, etc.

**Barrel Finishing:** A leaflet has been received from W. Canning and Co. Ltd., Birmingham, describing the Gallay mechanical finishing process. Use of this barrel process gives a bright finish to bulk quantities of articles varying in both size and shape. The finish obtained by this method is comparable to that achieved by manual methods and is an improvement on existing barrel processes. Articles may be plated without further polishing, and the company will process sample articles so that the results may be compared with existing polishing methods.

Polishing in General," by A. Brian, at the Grand Hotel, Sheffield. 6.30 p.m.

February 1

**Society of Chemical Industry (London Section).** "Surface Chemistry and Adhesion," by Dr. W. C. Wake, at Burlington House, Piccadilly, London, W.1. 6.30 p.m.

**Institute of Metal Finishing (Midlands Branch),** "Applications of Rubber and Plastic in Metal-Finishing Plant," by E. W. Mulcahy, at the James Watt Memorial Institute, Great Charles Street, Birmingham, 3. 6.30 p.m.

February 2

**Institute of Metal Finishing (Scottish Branch),** "Paint Finishes," by P. A. North, at the Institution of Engineers and Shipbuilders in Scotland, 39, Elmbank Crescent, Glasgow, 7.0 p.m.

February 3

**Institute of Metal Finishing (N.W.**

Branch). Paper by S. Wernick, Ph.D., M.Sc., F.R.I.C., F.I.M., at the Engineers' Club, Albert Square, Manchester. 7.30 p.m.

February 11

**Institute of Metal Finishing (Sheffield and N. E. Branch).** Annual Dinner and Dance at the Grand Hotel, Sheffield.

February 14

**Institute of Vitreous Enamellers (Southern Section).** Symposium on "Problems of Producing Coloured Acid-resistant Enamel Finishes," by Dr. B. K. Niklewski, C. P. Stokes and G. Evans, at the Howard Hotel, Norfolk Street, Strand, London, W.C.2. 7.15 p.m.

February 15

**Institute of Metal Finishing (Organic Finishing Group).** "Problems of a Paint Shop Controller," by R. M. C. Logan, at Regent House, Colmore Row, Birmingham, 3. 6.30 p.m.



# Latest Developments in

## PLANT, PROCESSES and EQUIPMENT

Fig. 1.—Plating barrels.

### Plating Barrels

THE Typhon plating barrel (Fig. 1) manufactured by W. Canning and Co. Ltd., Great Hampton Street, Birmingham, 18, has now had its design adapted to cover a range of three barrels, for capacities of 1 pint to 2 to 3 gallons. These barrels are simple to operate and have a built-in motor drive; they have an adjustable plating angle and are rotatable during emptying. A feature of the largest model is the incorporation of a pneumatic damper, to give a smooth return, after emptying, to the plating position. All three models are suitable for the deposition of most metals, except chromium, the two larger models—the "Master" and the "Major"—being suitable for bulk production. The "Minor" model is especially suitable for the deposition of precious metals, requiring only a small volume of solution.

### Dewatering Oil

A PRODUCT of Croda Ltd., Snaith, Goole, Yorks., is "Dewet" brand dewatering oil. It is a very thin, mobile, amber liquid, depositing a slightly soft, greasy, water-displacing film. The oil consists of a mixture of a soft grease-like material serving as a temporary anti-corrosive film former with special additives with dewatering properties and a volatile diluent. The oil has a flash point of 110 to 116° F., does not stain copper, and gives off no obnoxious fumes.

Although primarily evolved for application by dipping, brushing or spraying can be used.

### Aluminium Paint

THE Northern Aluminium Co. Ltd., have introduced two new grades of "Alpaste", viz., "Standard Polished" and "Standard Naphtha", and the names of all but one of the grades have been changed in order to make them more concisely descriptive.

### STANDARD POLISHED

**Special characteristics:** This grade satisfies the demand for an aluminium paste capable of producing a much brighter paint than the normal Standard grade. Its greater brilliance is of considerable value in decorative work,

while its durability is no less than that of the Standard grade.

**Formulation:** As the volatile content of Standard Polished consists chiefly of white spirit, this grade can be used in the same vehicles as Standard. However, the white spirit content is 8 per cent less than that of Standard and the metal content is accordingly greater, so that 8 per cent less Alpaste need be used in the vehicle, the difference being made up with white spirit or a solvent more suited to the particular paint. For most purposes a proportion of 2½ lb. of Standard Polished Alpaste to a gallon of vehicle will yield the best results.

### STANDARD NAPHTHA

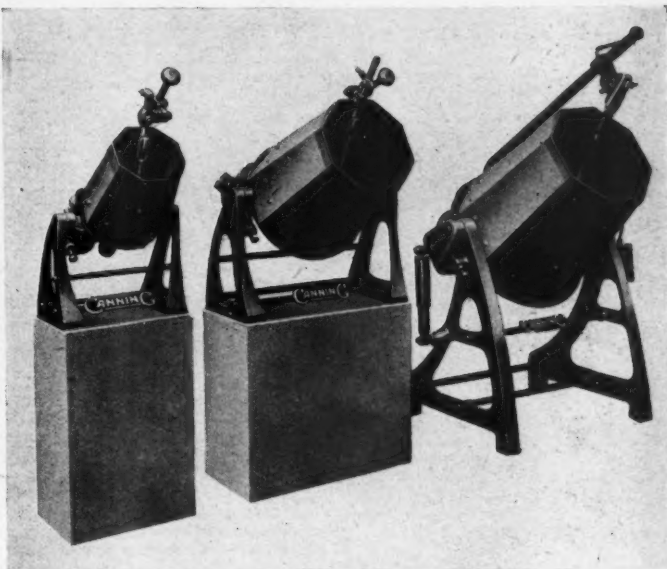
**Special characteristics:** This new grade is offered especially for use with modern synthetic paint vehicles not based on white spirit solvents. It is readily miscible in vehicles formulated from alkyl resins, vinyl resins, polysstyrene lacquers, nitrocellulose lacquers, chlorinated rubbers, silicone resins in xylol (for heat-resisting paints), and coal-tar pitches. While Standard grade can be used with some of these, the new Standard Naphtha is more

satisfactory and in many cases will give a smoother film. However, with some vehicles formulated from chlorinated rubbers, for example, it is essential to use Standard Naphtha; the only alternative is an aluminium powder pigment, over which the Alpaste pigment has the advantage of being easier and cleaner to mix and lower in cost.

Apart from the different solvents used in manufacture, the characteristics of Standard and Standard Naphtha are very similar.

**Formulation:** The best results are obtained with a proportion of 2½ lb. of this paste to a gallon of vehicle, giving 1.165 gallons of paint. Where Standard has previously been used, the same formulation can be applied to Standard Naphtha, and the same mixing technique observed: the vehicle should be added gradually to the Alpaste (not vice versa) with continuous stirring. Where mixing is likely to be troublesome, a little of the main solvent in the vehicle (e.g., xylol, toluol) should first be mixed into the Alpaste.

It has been decided to revise the names of the Alpaste products to make them more descriptive and



rational. Thus, the word "standard" in the name refers to one particle size, "ink" to another (finer) size, and "fine" to the finest of the range. The following table gives the revised nomenclature for all the grades and a short note on the typical uses of each:

| New name             | Old name                       | Typical uses   |
|----------------------|--------------------------------|--|
| Standard             | Standard                       | The pigment most often used for general paint work. Conforms to BSS.338.   |
| Standard Polished    |                                | Similar to Standard, but giving finishes of greater specular brilliance and smoother paint films in varnish vehicles. Particularly useful for decoration.  |
| Standard Naphtha     |                                | For paint in lacquers and synthetic vehicles. Particularly suitable for bituminous aluminium paints having a coal-tar pitch base. Can readily be mixed with nitrocellulose and synthetic resin vehicles which have low tolerance for aliphatic hydrocarbons. |
| Standard Non-leaving | Non-leaving                    | Similar to Standard except that it does not leaf; gives a pleasing metallic finish. Most suitable in primers for wood-work and other absorbent materials, composite primers for steel and intermediate coats for all surfaces.                               |
| Ink                  | Ink H                          | Much finer than Standard. Commonly used in silver ink for letterpress and lithographic printing.   |
| Fine                 | Extra-fine Lining              | Used in special-purpose paints and in inks for superfine printing. Gives a more enamel-like finish than Standard or Ink.   |
| Fine Non-leaving     | Extra-fine Lining, Non-leaving | Chiefly used for polychromatic and hammer finishes.  |

#### Motors for the Chemical Industry

THE English Electric Co. Ltd. is now manufacturing a range of squirrel-cage induction motors specially designed for operation in the corrosive but non-explosive atmospheres found in installations such as chemical plants, plating shops, gas works, coke plants, salt works and oil refineries. The motors are made to British Standard dimensions and are available in outputs up to 25 h.p. Although similar in appearance to the normal "English Electric" class LY totally enclosed, fan-cooled machines, these motors incorporate many unique features (Fig. 2) that resist the corrosion caused by such things as

Fig. 2. — Motors for the chemical industry.

excessive humidity, salt air and sulphur dioxide fumes.

A moulded plastic fan (A), mounted on the non-driving end of the shaft, cools the motor by blowing air along axial cooling fins cast integral with the motor frame (B). The fan is made from phenol-formaldehyde, and durability and fatigue tests have been carried out to prove the suitability of this material and also the special method of fixing the fan on the shaft. After tens of thousands of stress reversals, simulating the severest conditions of duty that could be imposed on a motor, the fans have remained undamaged and secure.

Polyvinyl-acetate-covered wire is used for the stator winding (C). The windings are impregnated with phenolic insulating varnish by dipping and baking them four times in an automatic heat-controlled continuous oven; this process has been found to produce a finished winding capable of high resistance to corrosive chemicals.

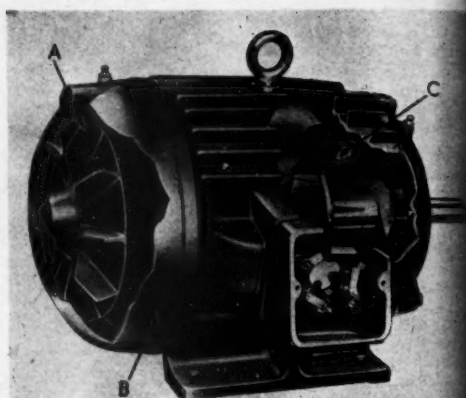
Wherever possible, cast iron is used for components forming the external surfaces of the motors. The cowl over the fan is also made of cast iron instead of pressed-steel, and all external surfaces of the stator and the fan cowl are finished with a special protective paint.

The rating plate is made from polyvinyl chloride to ensure that it is not obliterated by corrosion.

#### Germanium Power Rectifier

THE British Thomson-Houston Co. Ltd., recently announced that they have put into service in their Rugby Works a germanium-type rectifier rated at 300 kw., 1,100 amperes. This, as far as is known, is the first application of germanium on this side of the Atlantic to the problem of power rectification. A new rectifier characterized by extremely high efficiency is thus entering a field normally covered by mercury-vapour devices or rotating machinery. The efficiency of this first equipment is 98.5 per cent and it is likely that further equipments will show an even better performance.

Day-to-day experience with this first successful unit is being recorded; but it should be realized that before the use of germanium on a wide scale for power rectifying devices can be



accomplished, there is a great deal more work to be done. Units of new designs and different capacities must be produced at the laboratory stage, and the suitability of germanium as a rectifier for different types of service must be carefully considered. A further unit on a different type of service will be installed shortly in the BTH company's works, and it is hoped that during 1955 two more equipments will be installed to try them out in more severe service conditions. The rectifying units for each of these will be produced in the laboratory.

The time is therefore not ripe for quantity production. It is, however, expected that progress during the second year of the development will be commensurate with that made during the first year, and if this expectation is realized, a means of power rectification at high efficiency will soon become available to meet industrial needs.

The current/voltage characteristic curve of a 50-ampere rectifier unit shows that at a current of 50 amperes the voltage drop is less than 1 volt.

#### Lightweight Protective Aprons

HIGHER resistance to abrasion, chemicals and water, longer service life and increased comfort in use due to reduction in weight of material are some of the features of the new P.V.C. protective aprons introduced recently by James North and Sons Ltd., Kirkman House, 54a, Tottenham Court Road, London, W.1. The material used is a hard-wearing fabric impregnated and proofed by the company's formulation of P.V.C. The "tack-free" surface minimizes retention of dirt, and the material does not perish. For work involving excessive abrasion, additional protection can be provided by a reinforcement patch on the front of the garment. These aprons are available in a range of sizes and are fully adjustable by means of shoulder straps.

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